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of the Hungarian Academy of Sciences**

Structure and Properties of Carbon Based Nanocomposite Films

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Outline

Introduction

Experimental

Results and discussion

Conclusions



1. INTRODUCTION

The theoretically predicted superhard $\beta\text{-C}_3\text{N}_4$ has not yet been experimentally realized, however, the different CN_x structures and their applications is a reality.

Presently the research is focused on *fullerene-like* CN_x thin films. They are modestly hard (max. 18-20 GPa) compared to nowadays' superhard coatings, (30-40 GPa) and have a fairly high elastic modulus (130-200 GPa). The most interesting properties of fullerene-like films are their extreme elasticity (nearly 90% elastic recovery) and good wear resistance with a friction-coefficient similar to nonhydrogenated diamond-like carbon (DLC).

In this talk the structure, morphology and the mechanical properties of d.c. magnetron sputtered nanocomposite films of carbon or CN_x matrix and nickel as dispersed component are investigated. Our main interest was the influence of the nickel on the structure of the C/CN_x matrix and its relation to nanohardness of the composite layers.



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Superhard coatings: 40 GPa

Diamond: 70-100 GPa, Cubic BN: 50 GPa

Nitride nanocomposites (e.g.) TiN in Si₃N₄): 50-100 GPa

Electroplated Cr: 12 GPa

TiN: 23-25 GPa

TiCN, TiAlN, TiZrN: 33 GPa

C/Cr: 27 GPa

Nitride multilayers (TiN, VN, AlN, NbN, CrN): 35-50 GPa



2. EXPERIMENTAL :

Sputtered films: CN_x and C (+ Ni) films were prepared at 30-800 °C on substrate temperature in $(2-3) \times 10^{-3}$ mbar Ar-ban vagy N_2 -ben.

Background pressure: 2×10^{-6} mbar.

Nitrogen, Argon: 99.9999 % (V/V).

Targets: high purity (99,5%) pyrolytic graphite.

Substrates: oxidised (100)Si, glass, NaCl

Mechanical measurements

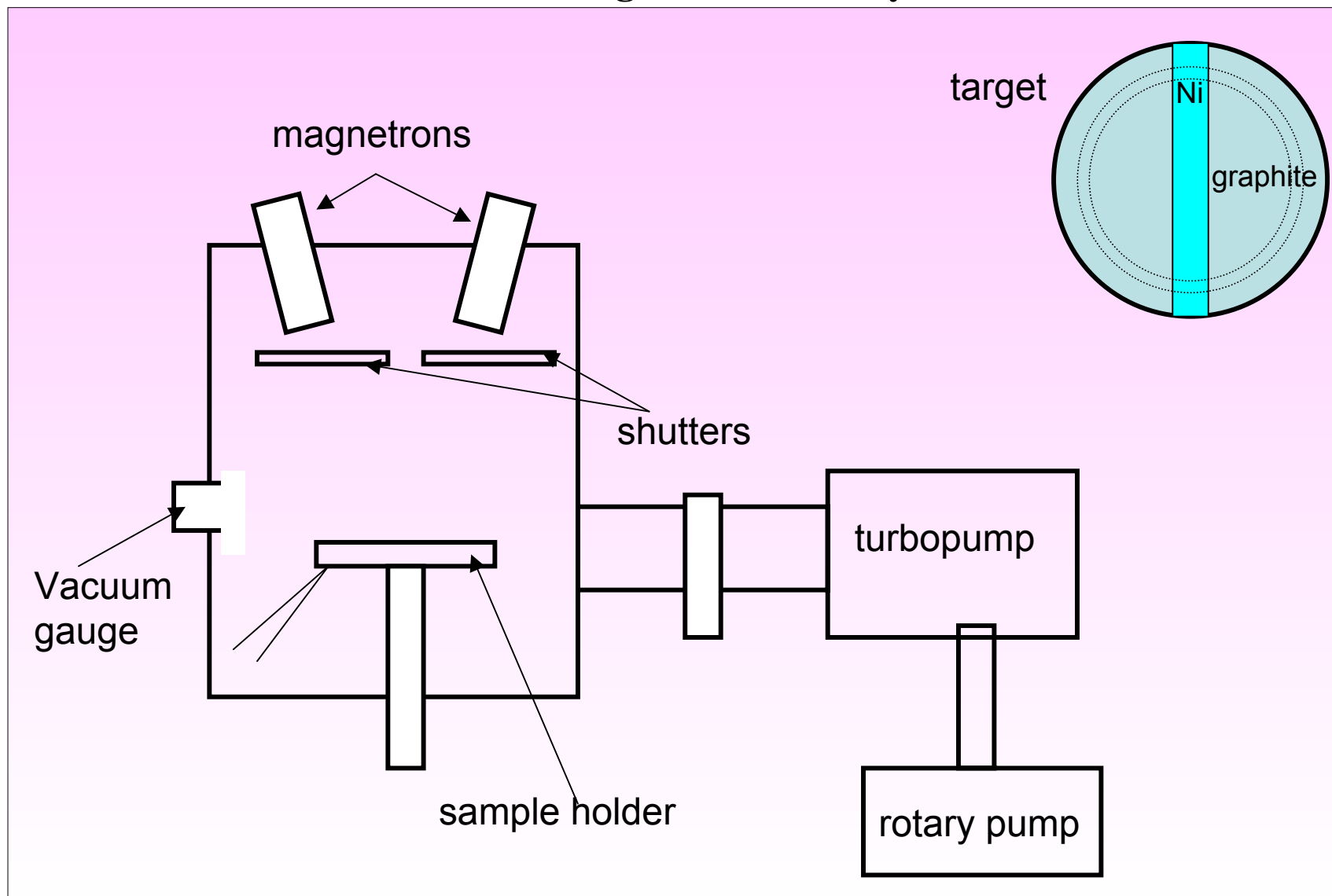
Dynamic nano-hardness and friction coefficient were measured by a NanoTest 600 nano-mechanical tester (Micro Materials Ltd., UK).

A Berkovich type indenter-head was applied for hardness measurements in depth control mode with a penetration depth of 50 nm.

A 'Sharp Rockwell' head was used for friction tests with 1 micron/sec velocity and 3 mN load.



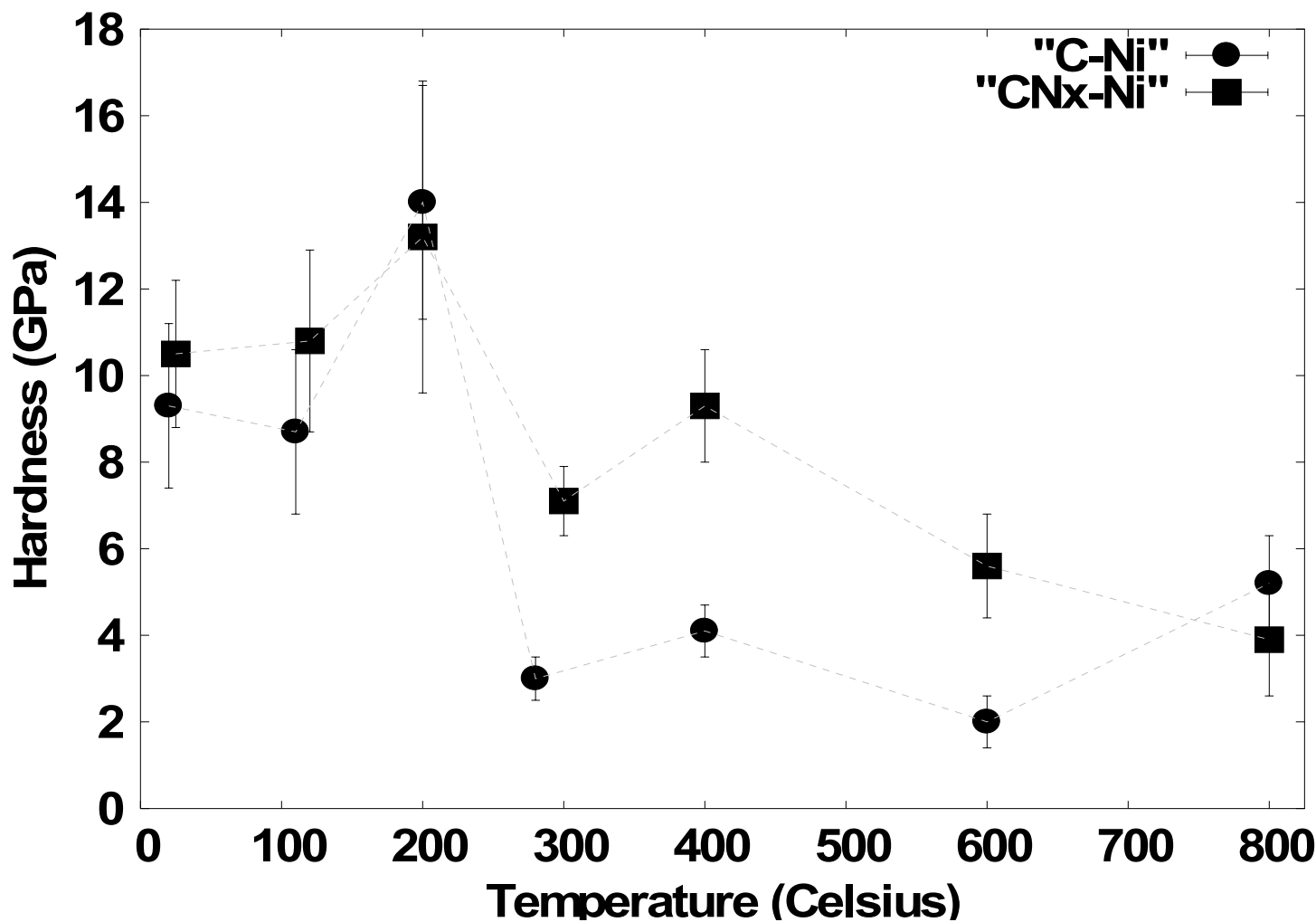
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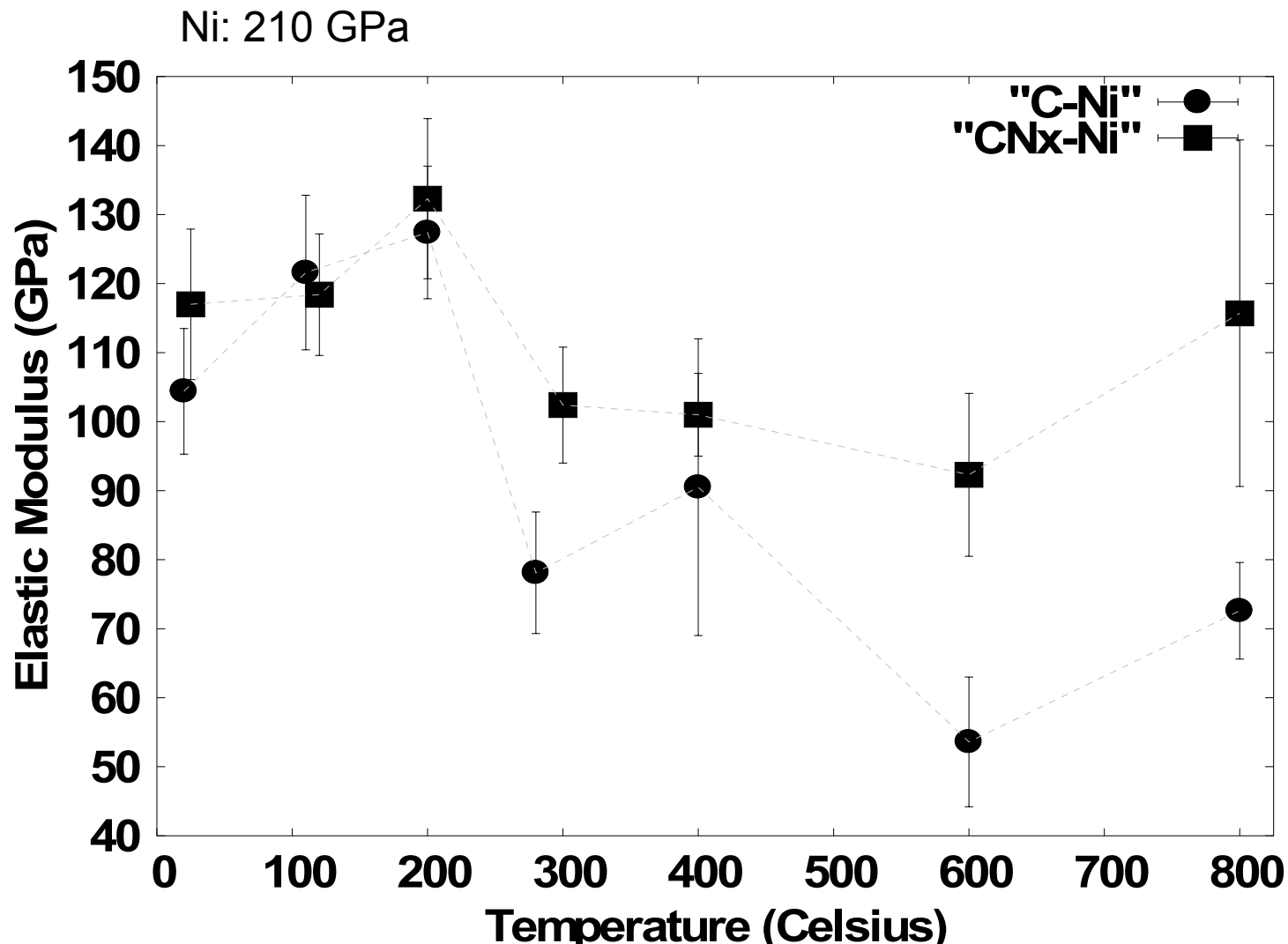
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3. RESULTS



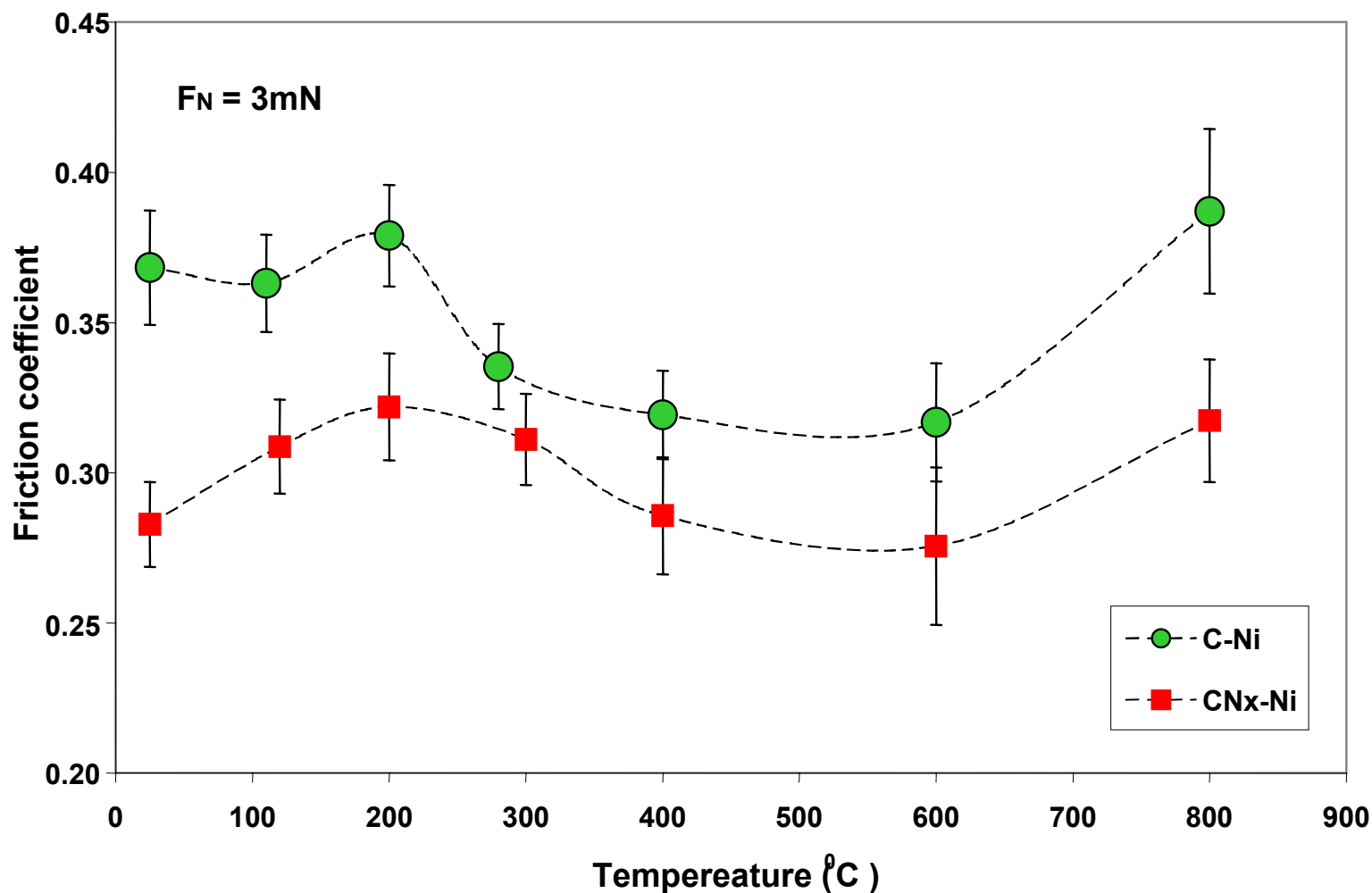


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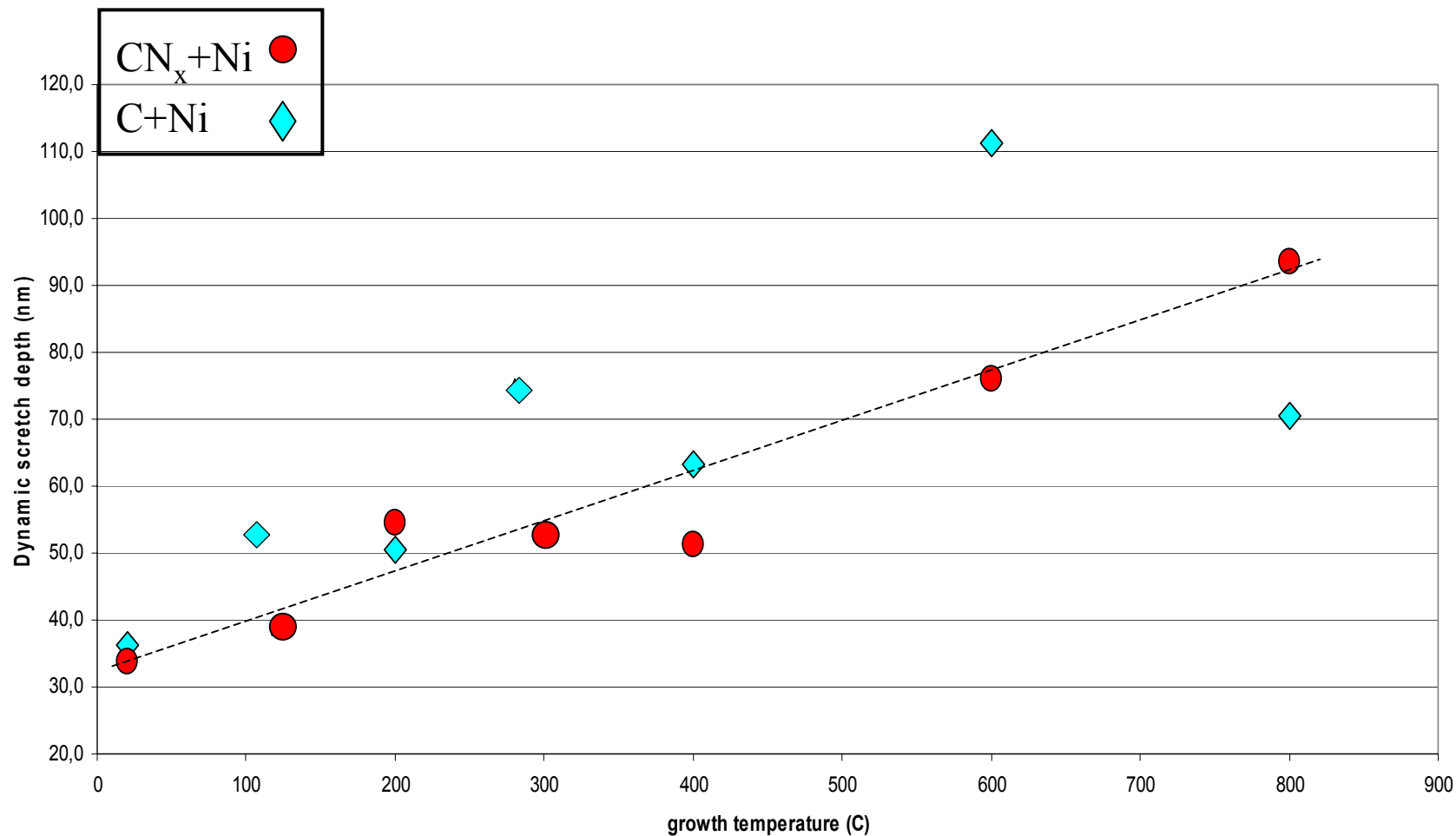
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A 'Sharp Rockwell' head was used for friction tests with 1 micron/sec velocity and 3 mN load.

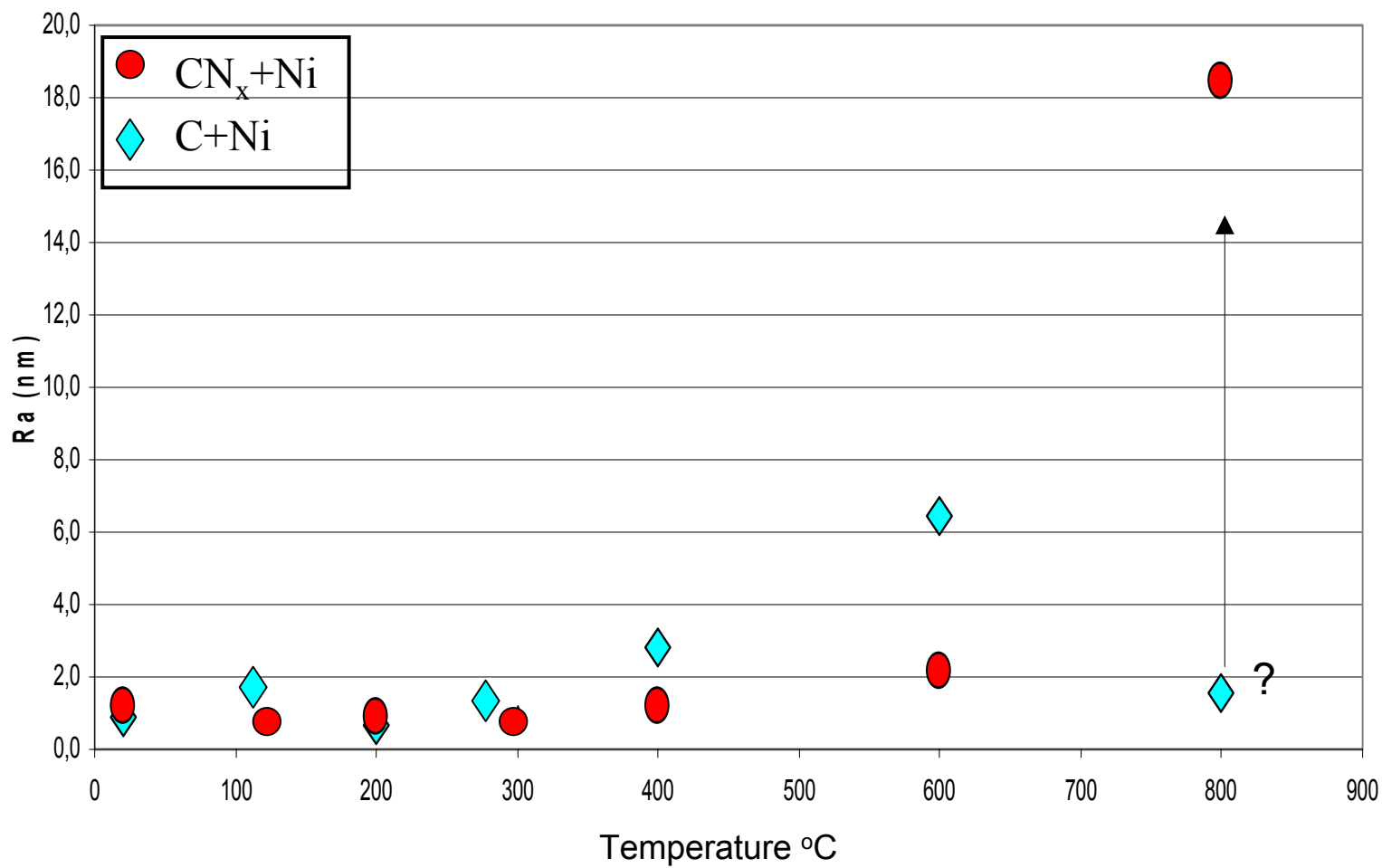


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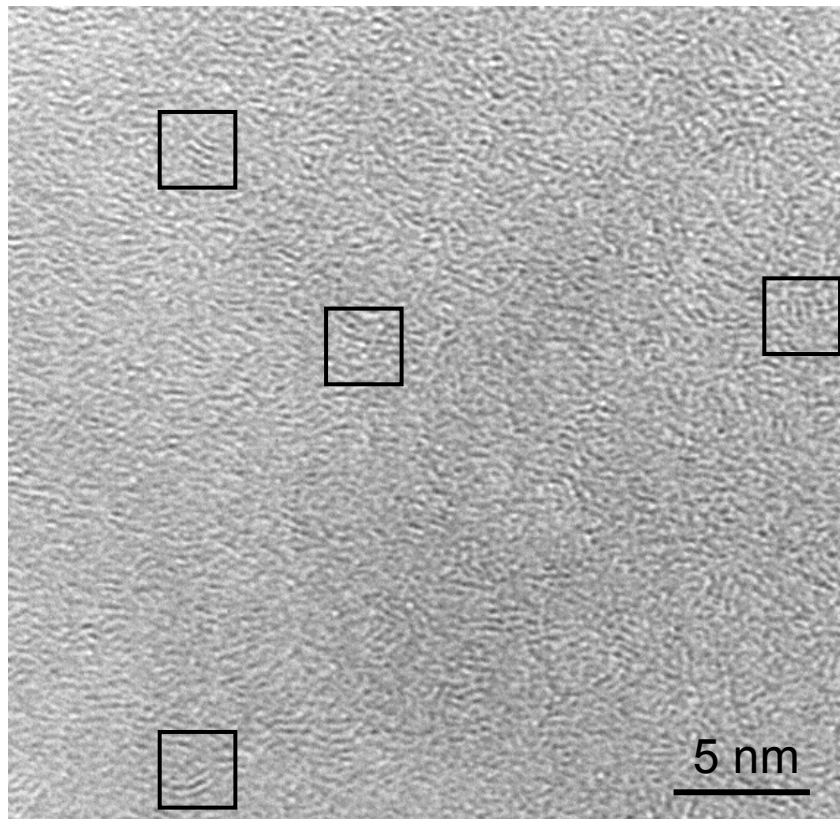


Roughness as the function of the deposition temperature

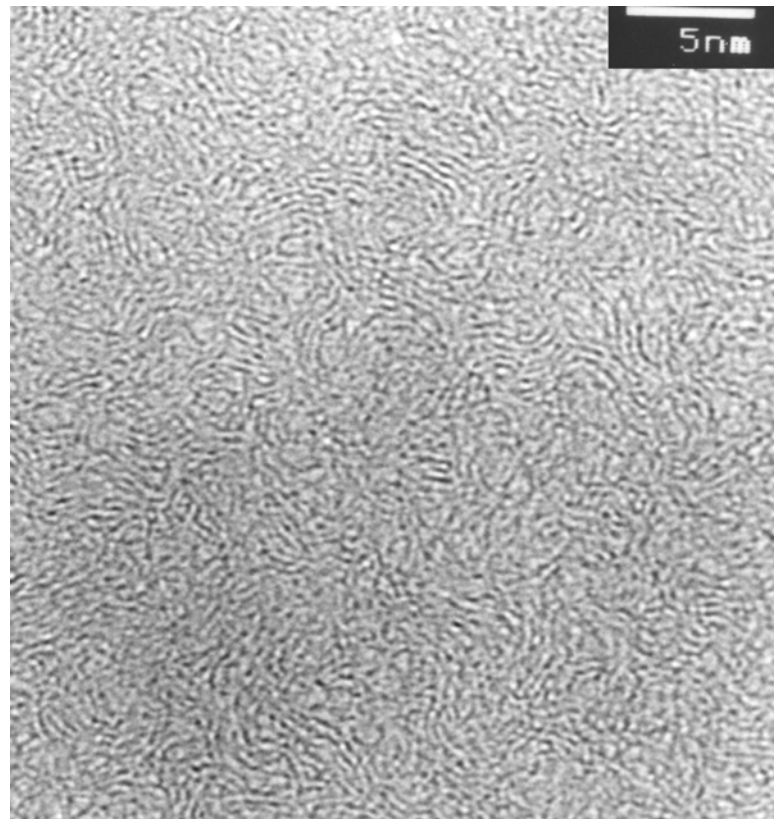


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The effect of substrate temperature on the ordering of carbon

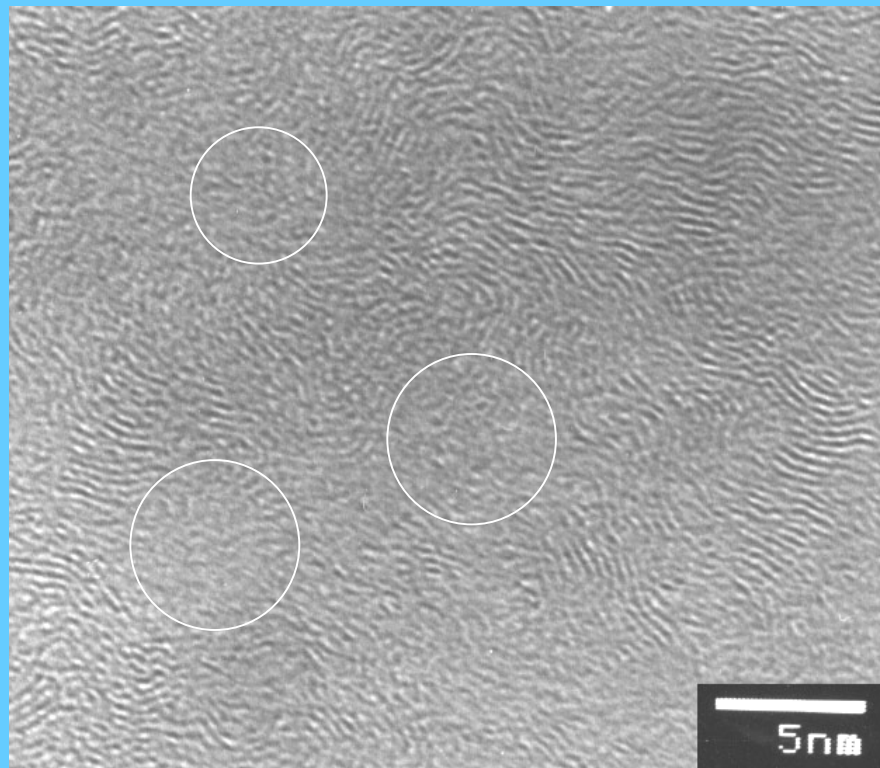


CNM11 (C in Ar, RT, SiO₂, NaCl)



and CNM13 (C in Ar, 400°C, SiO₂)

The structure of CN_x prepared at high temperature



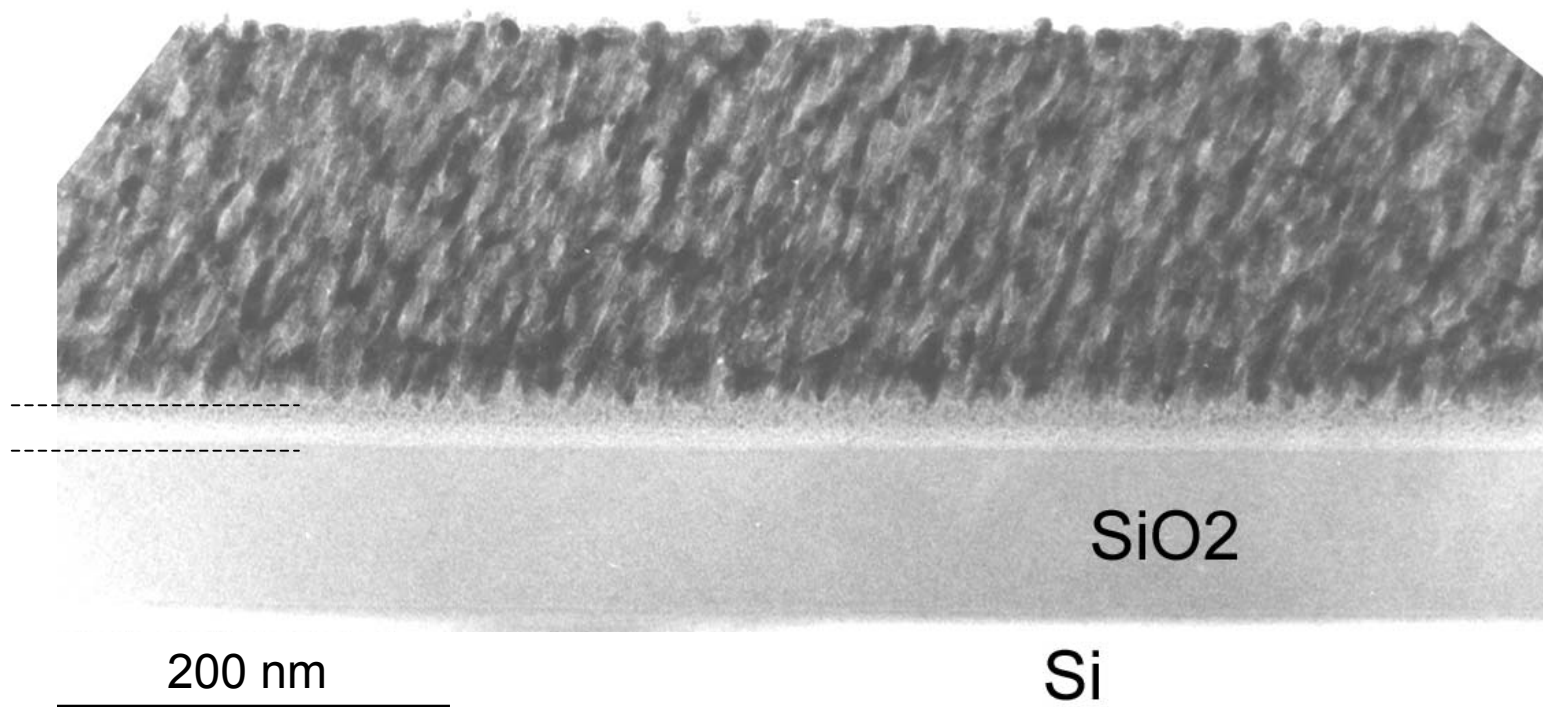
CN_x , N:6 at%

800°C/ SiO_2

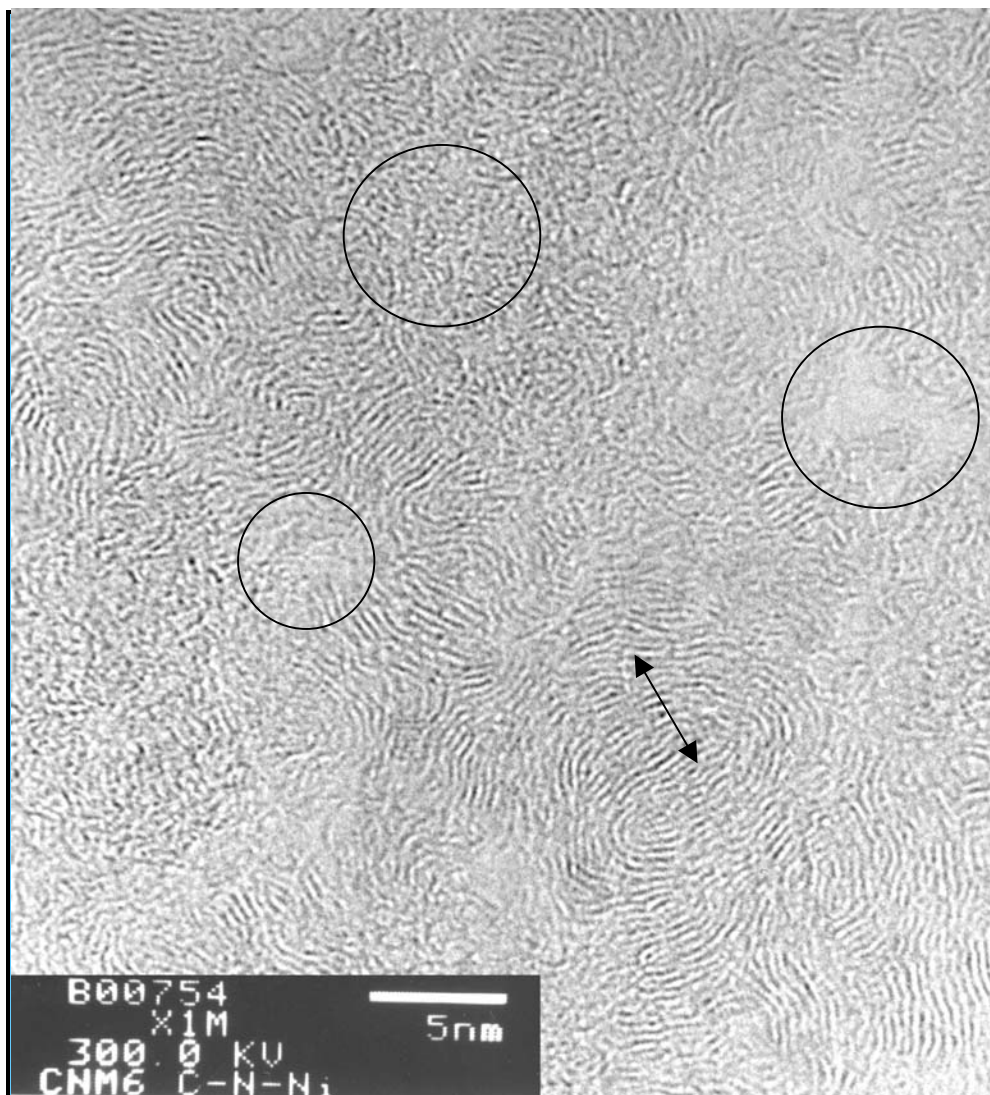
22 nm thick



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RT, C+N+Ni



The effect of Ni addition

CN_x-Ni nanocomposite,
prepared by DC
magnetron sputtering.

7×10^{-7} mbar

700°C, Si substrate

N₂, 2×10^{-3} mbar

$t = 36$ nm; 0,5 nm/s

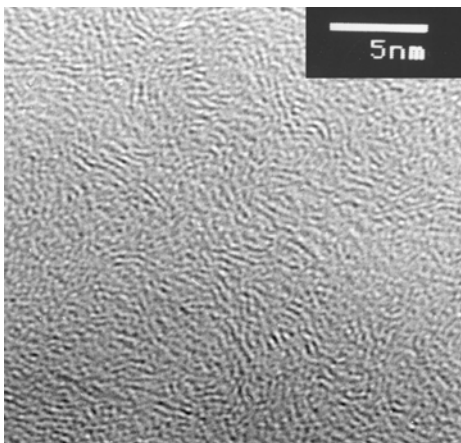
N: about 10 at%

Ni: <0,5at% dissolved by HF

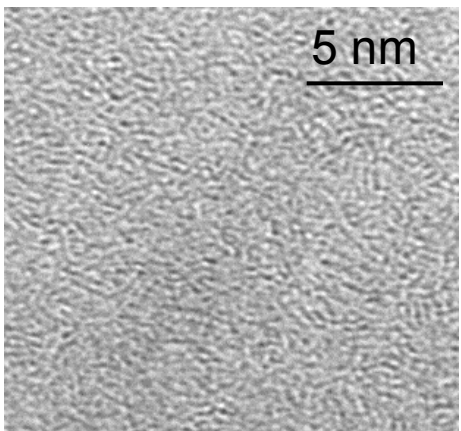
CNM6



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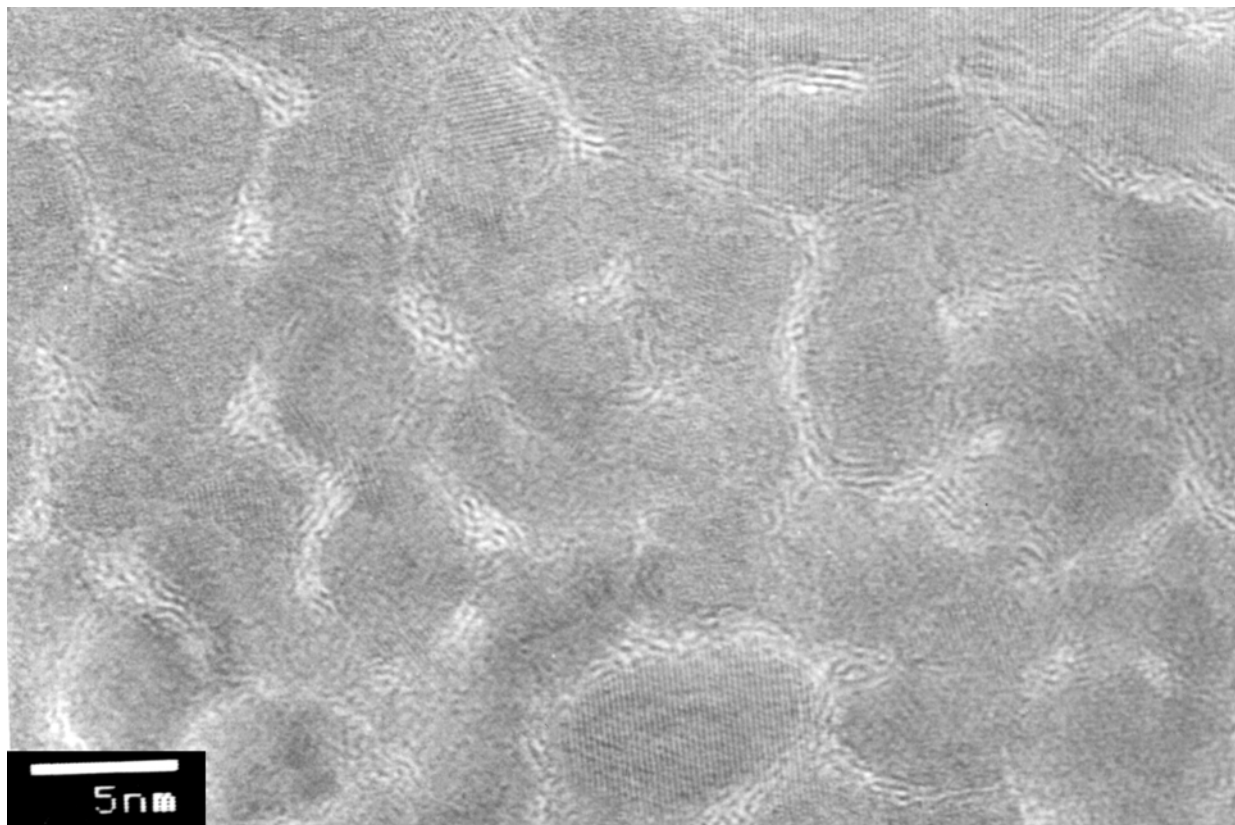


C in Ar 10 nm, SiO₂
Ts=600°C CNM14

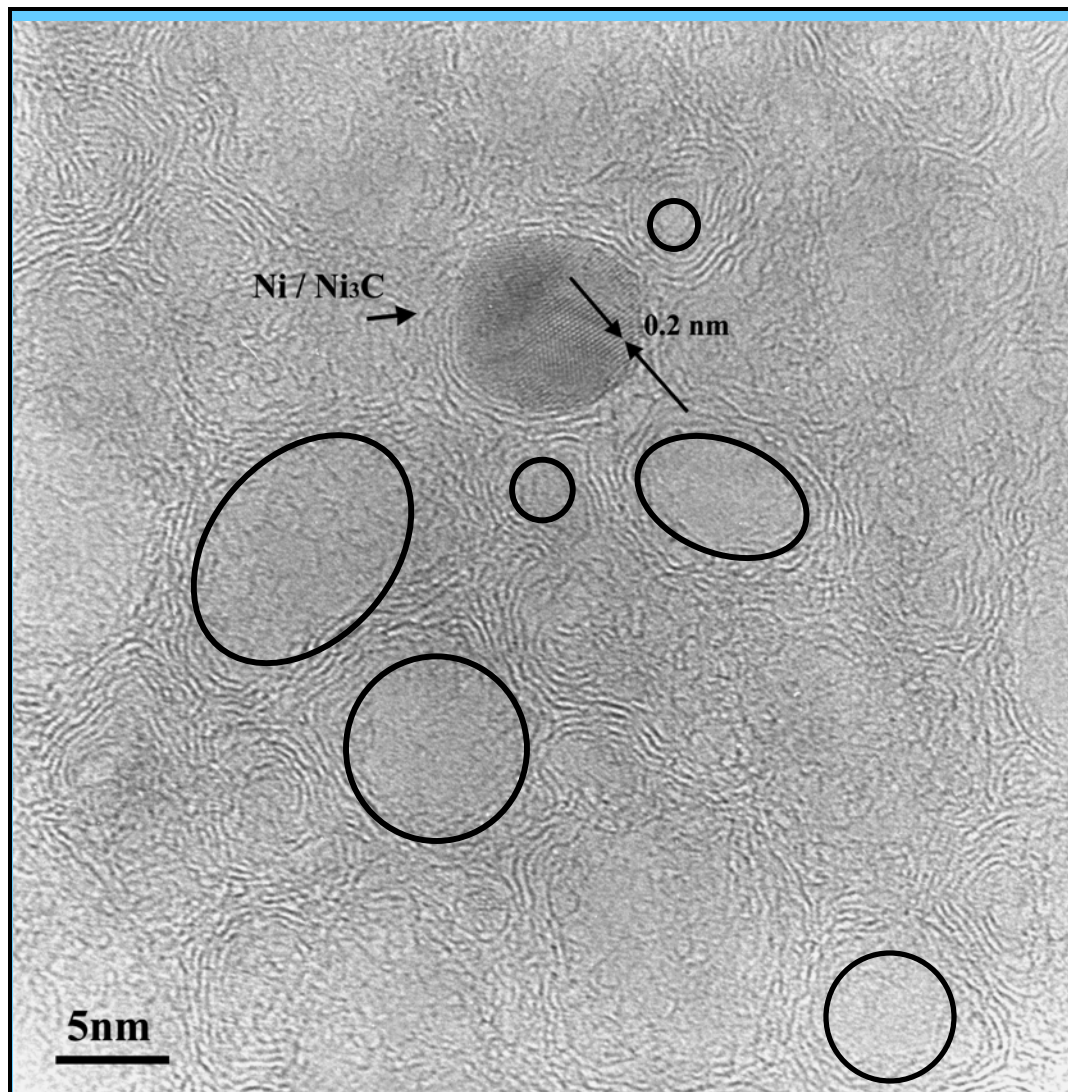


(C in Ar, RT, NaCl)

CNM11



C+Ni, RT, 20 nm



CNM20 C+Ni

600 °C /SiO₂ substrate

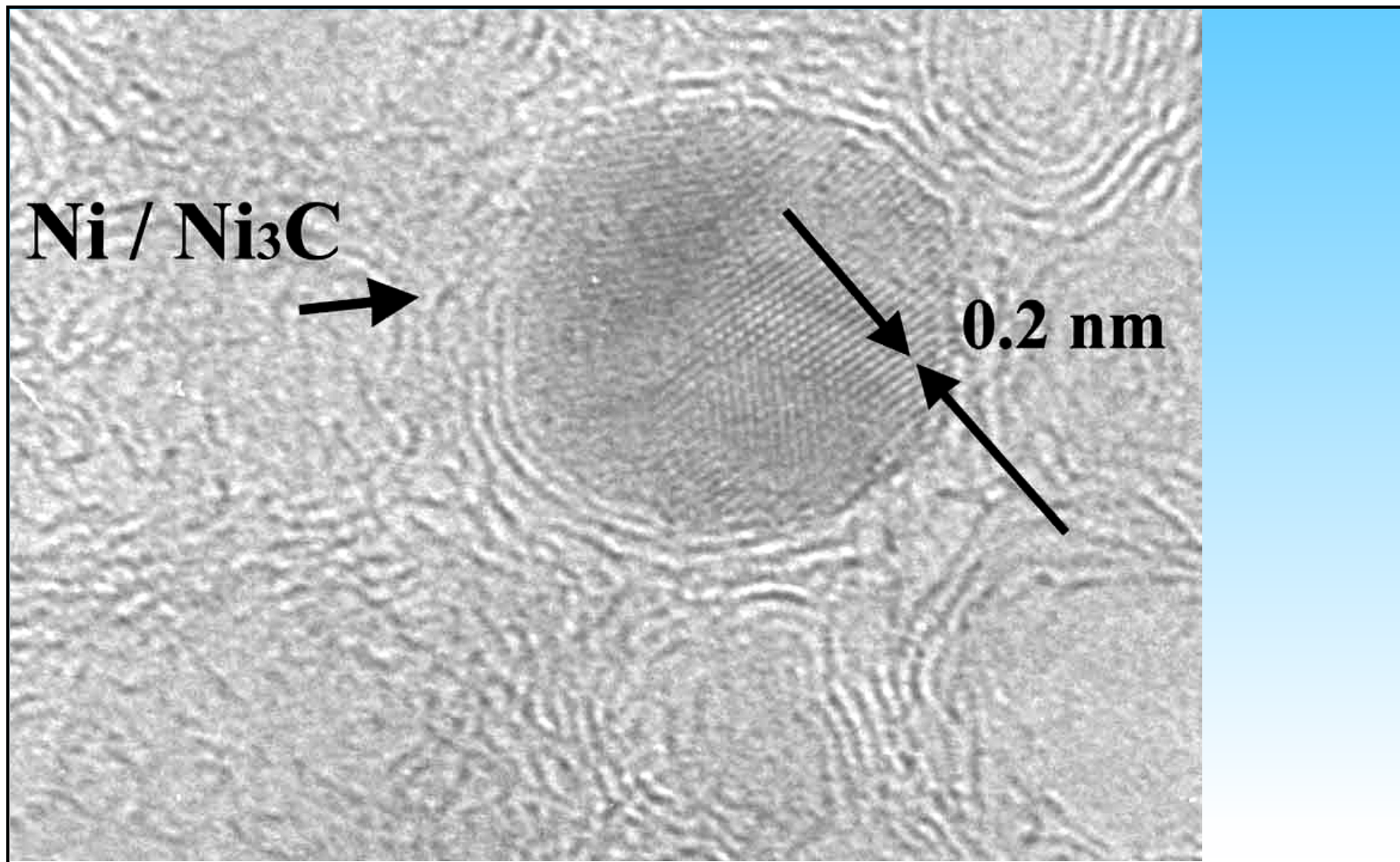
15 nm thick C/Ni
nanocomposite.

Ni/Ni_xC dissolved by HF.

The contours mark the places of
some dissolved particles.

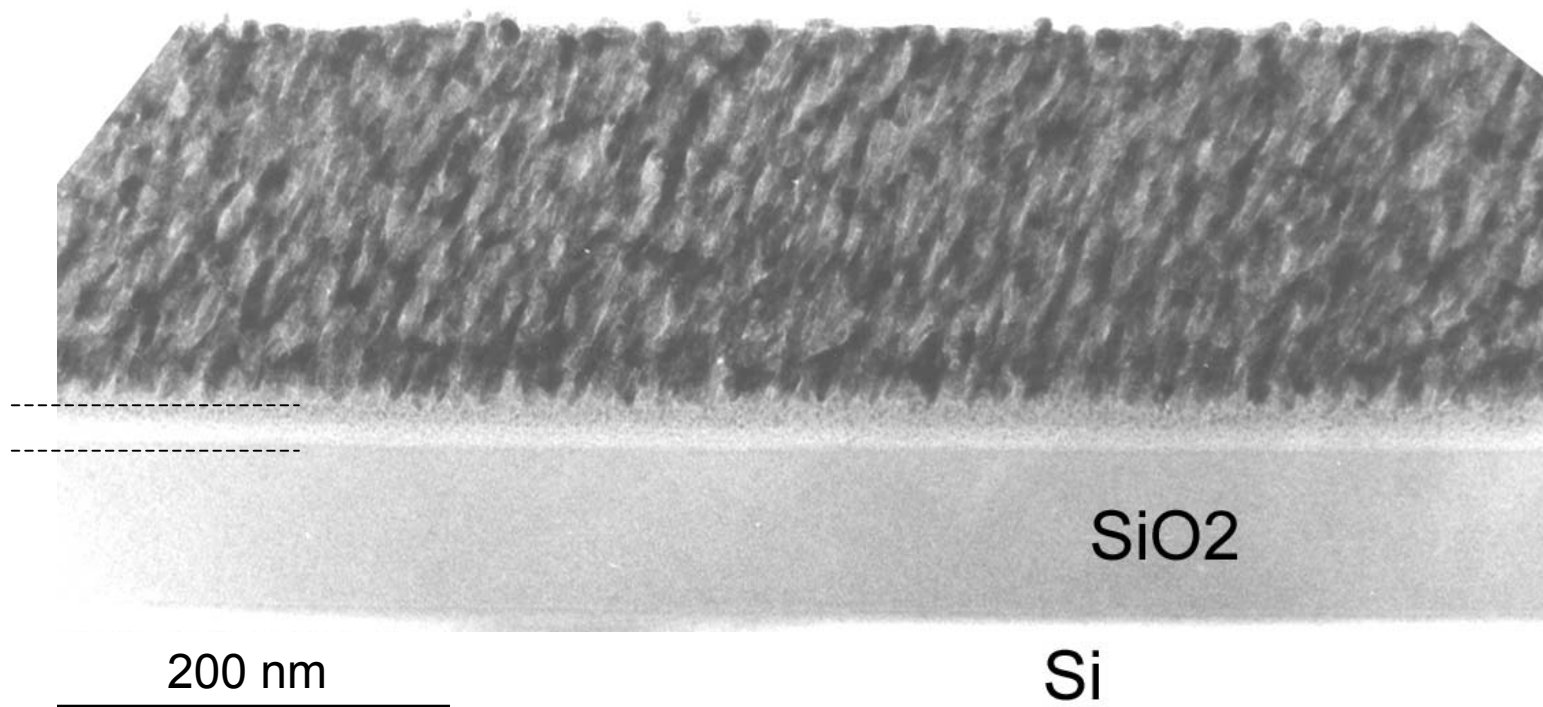


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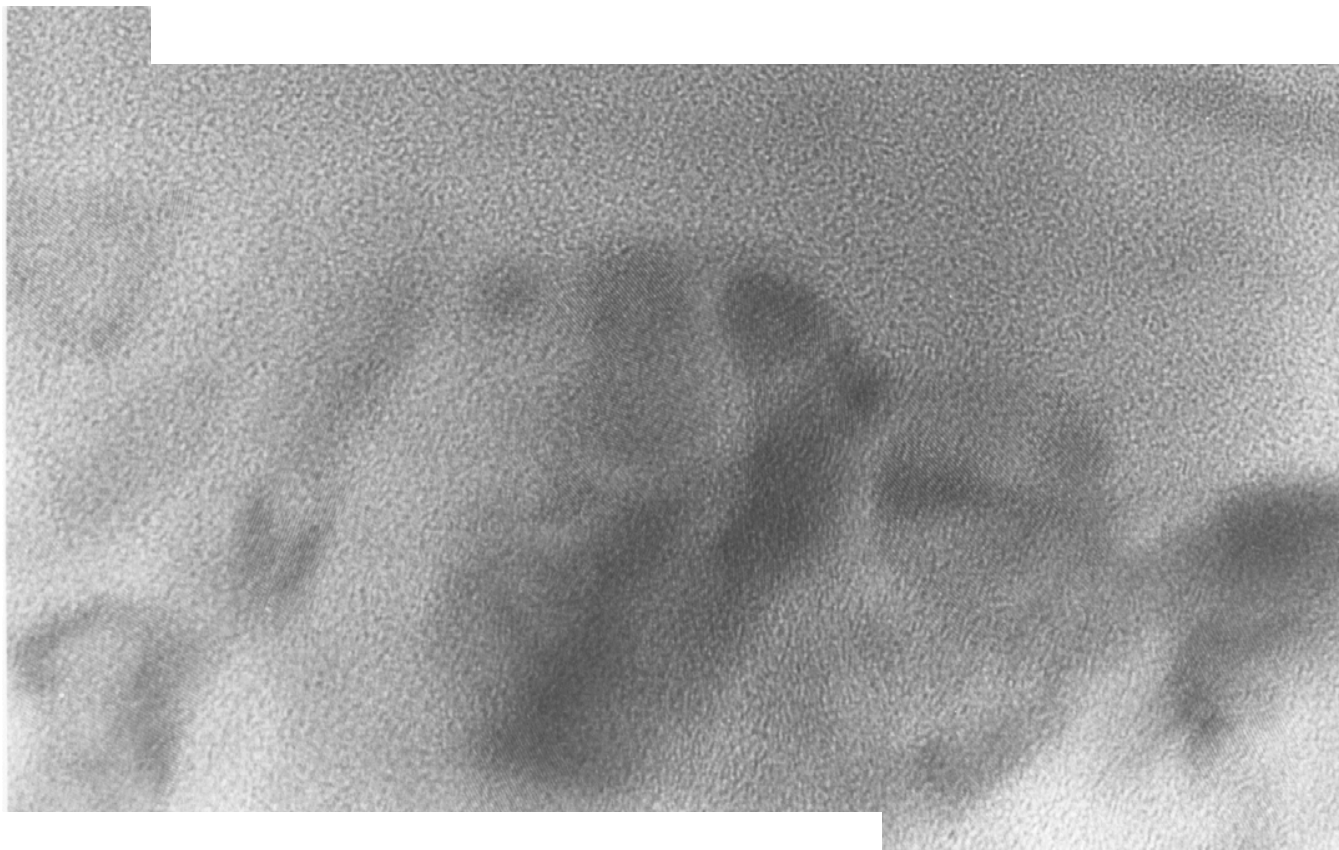
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RT, C+N+Ni



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IM29

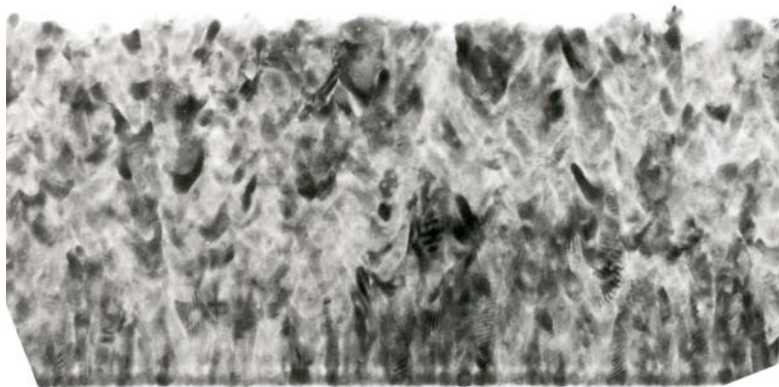
10 nm



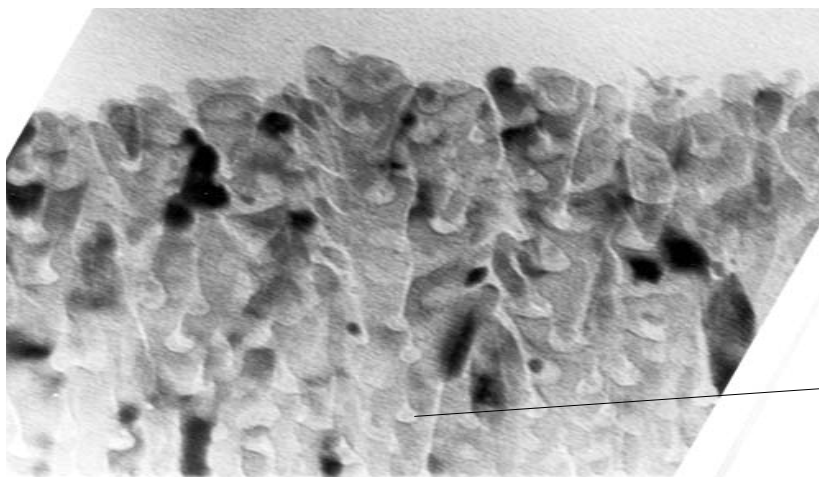
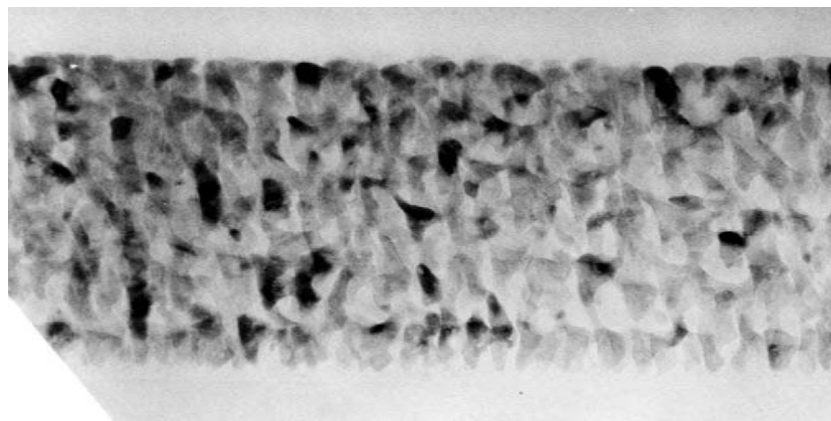


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CNM36, 120°C, 250 nm

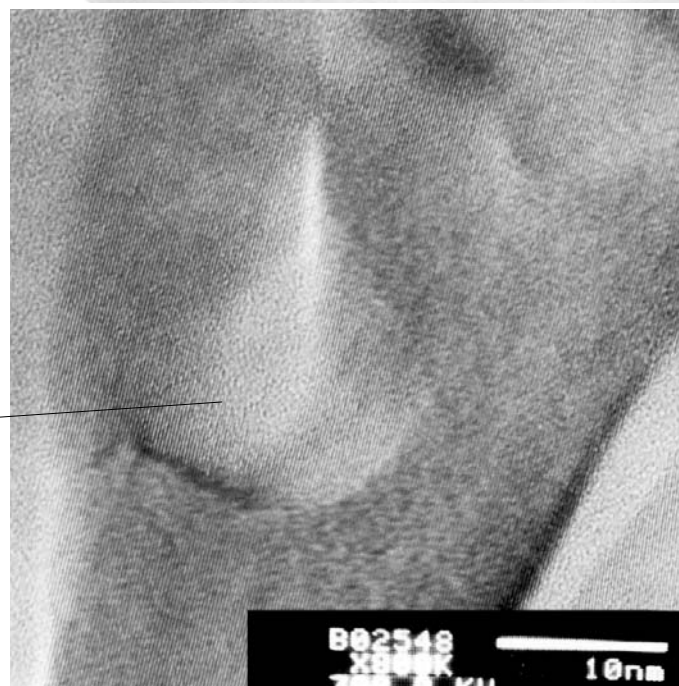


CNM30 200°C 230 nm



250 nm
CNM37 300°C, 300 nm

C+N+Ni



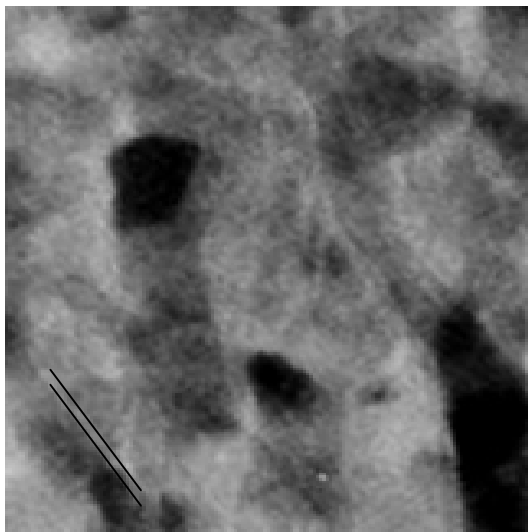


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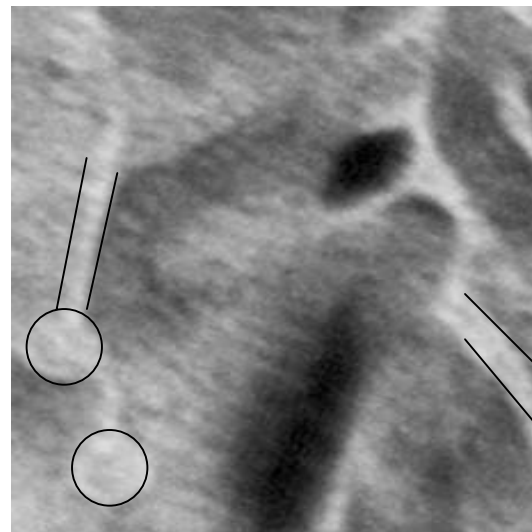
120°C



200°C



300°C



2 nm

$2 \text{ nm} > t$

$d \sim 2 \text{ nm}$

$2 \text{ nm} > t$

$d \sim 2-4 \text{ nm}$

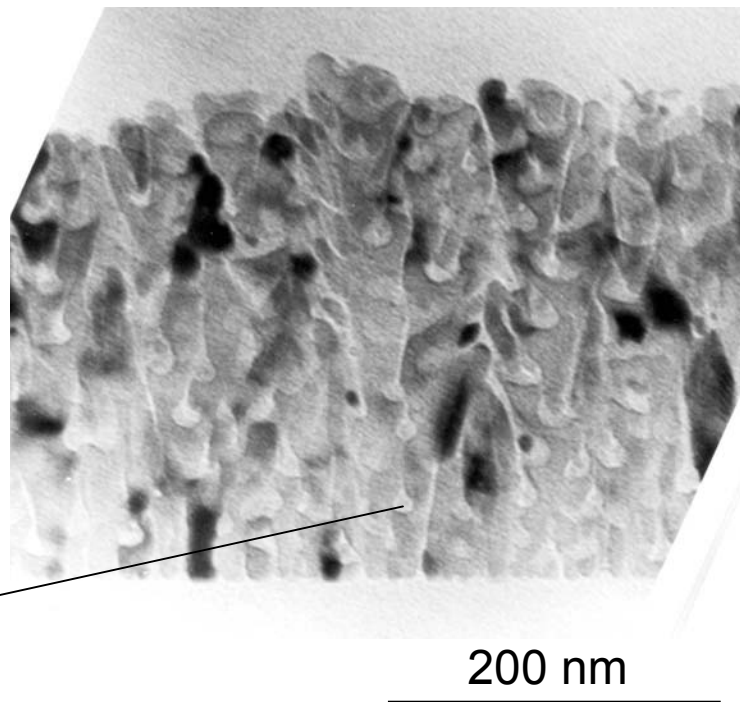
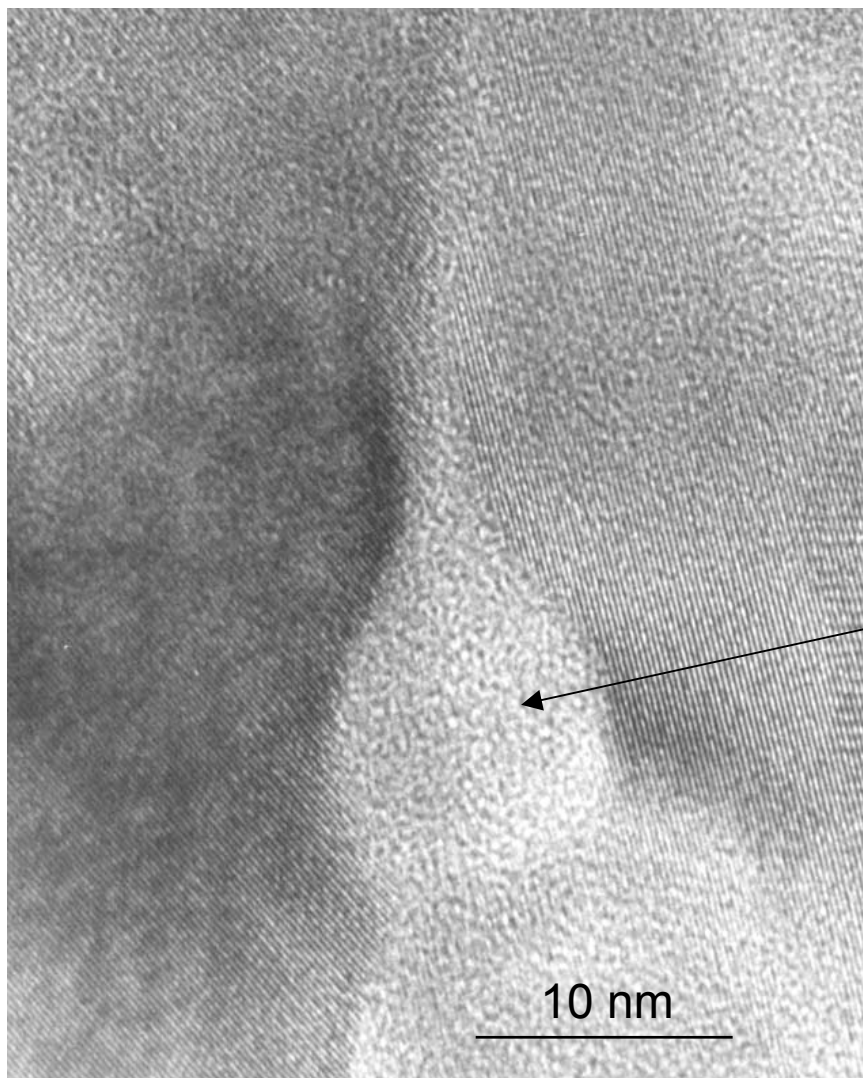
$t = 2-5 \text{ nm}$

$d \sim 10 \text{ nm}$

C+N+Ni

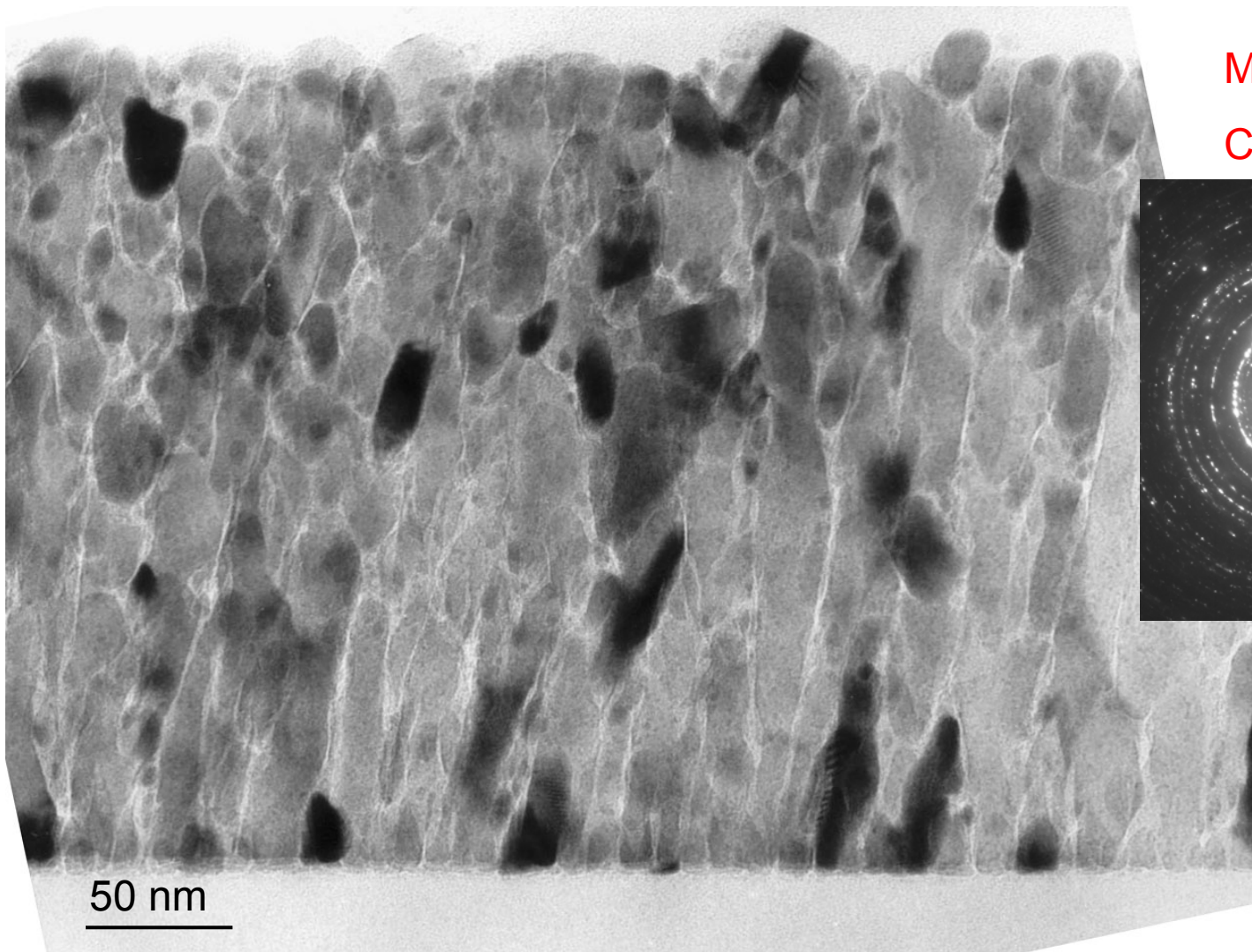


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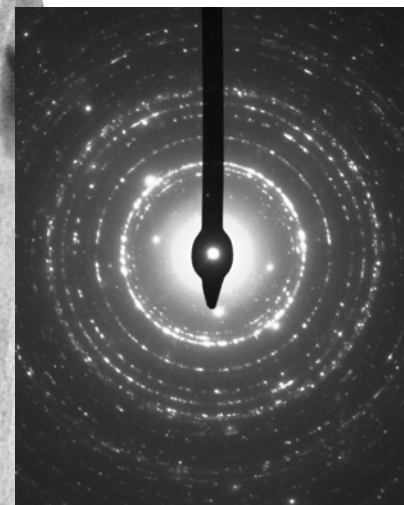
C+N+Ni

CNM37 300°C, 300 nm



Morphology

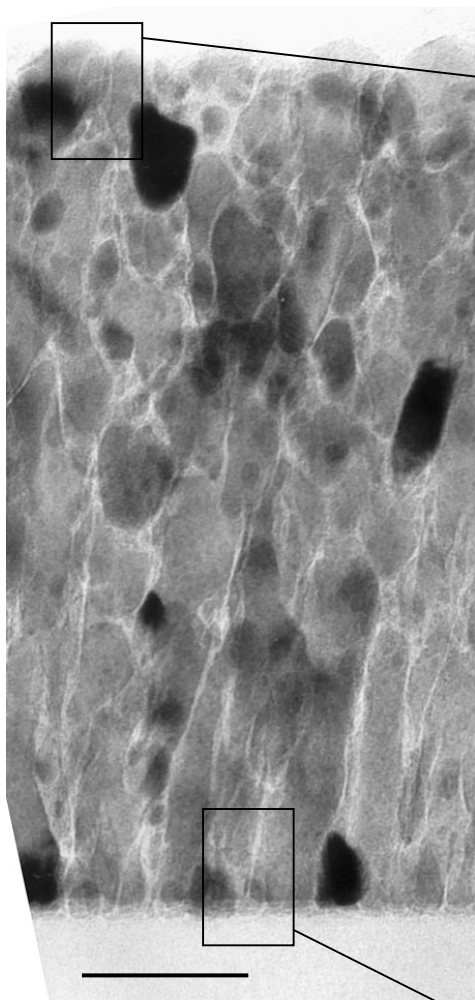
Cryst. phase



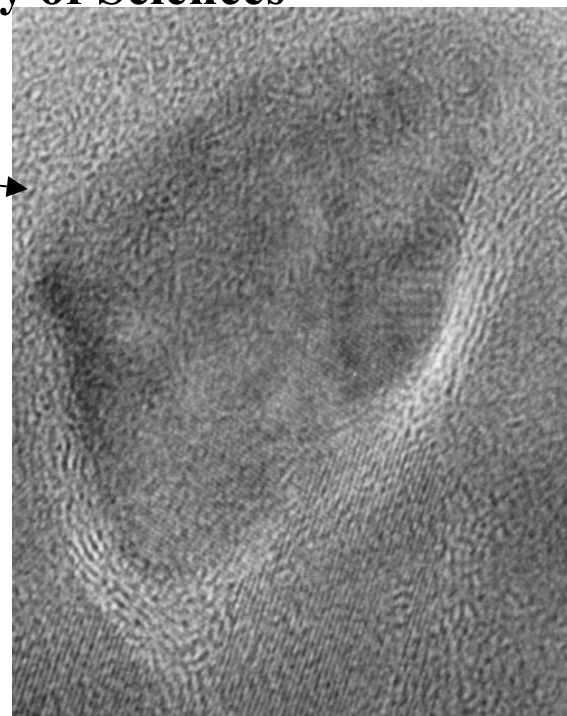
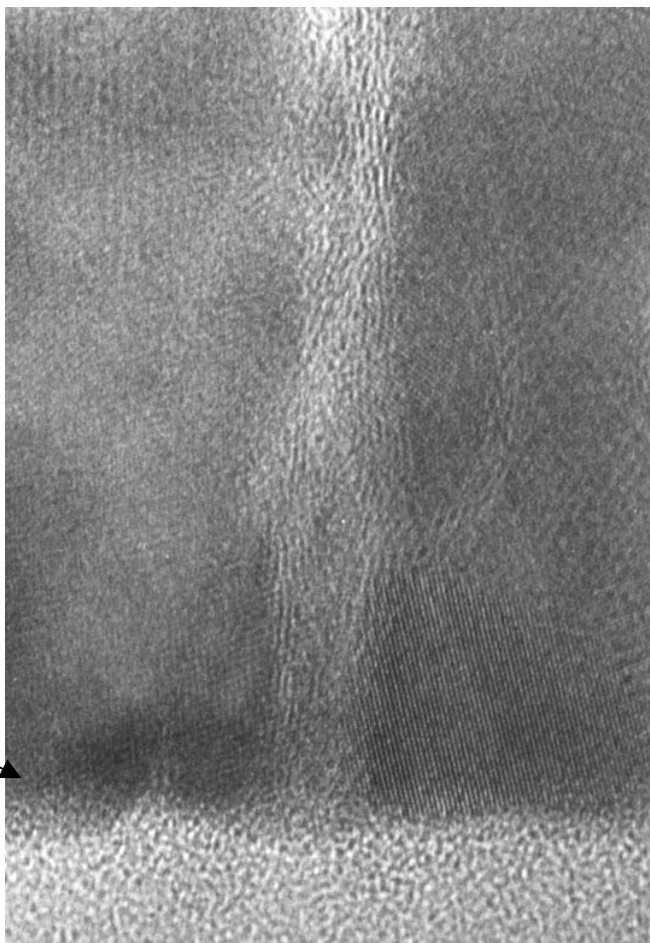
200°C, Si+SiO₂ substrate, C+Ni



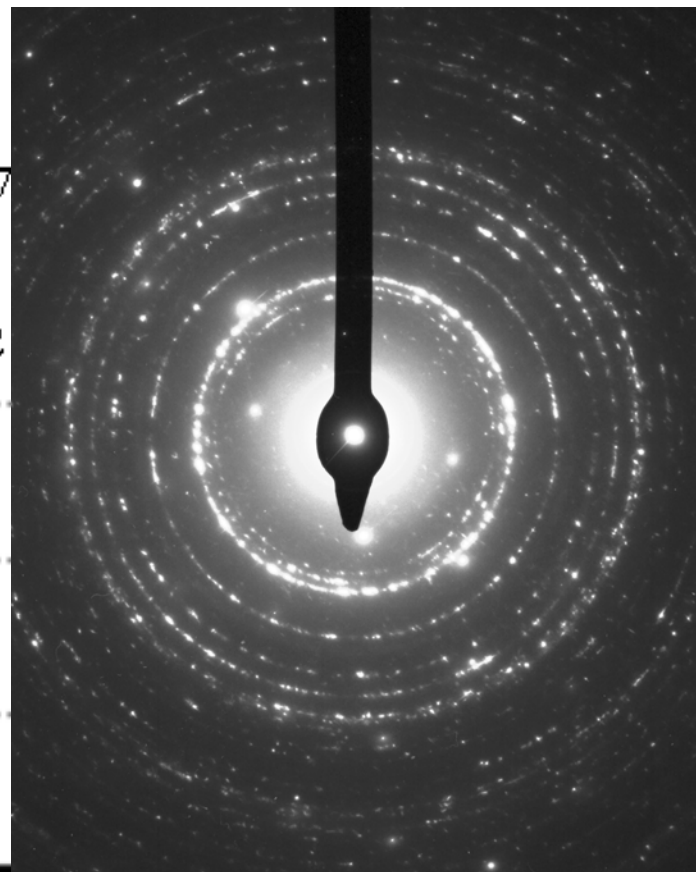
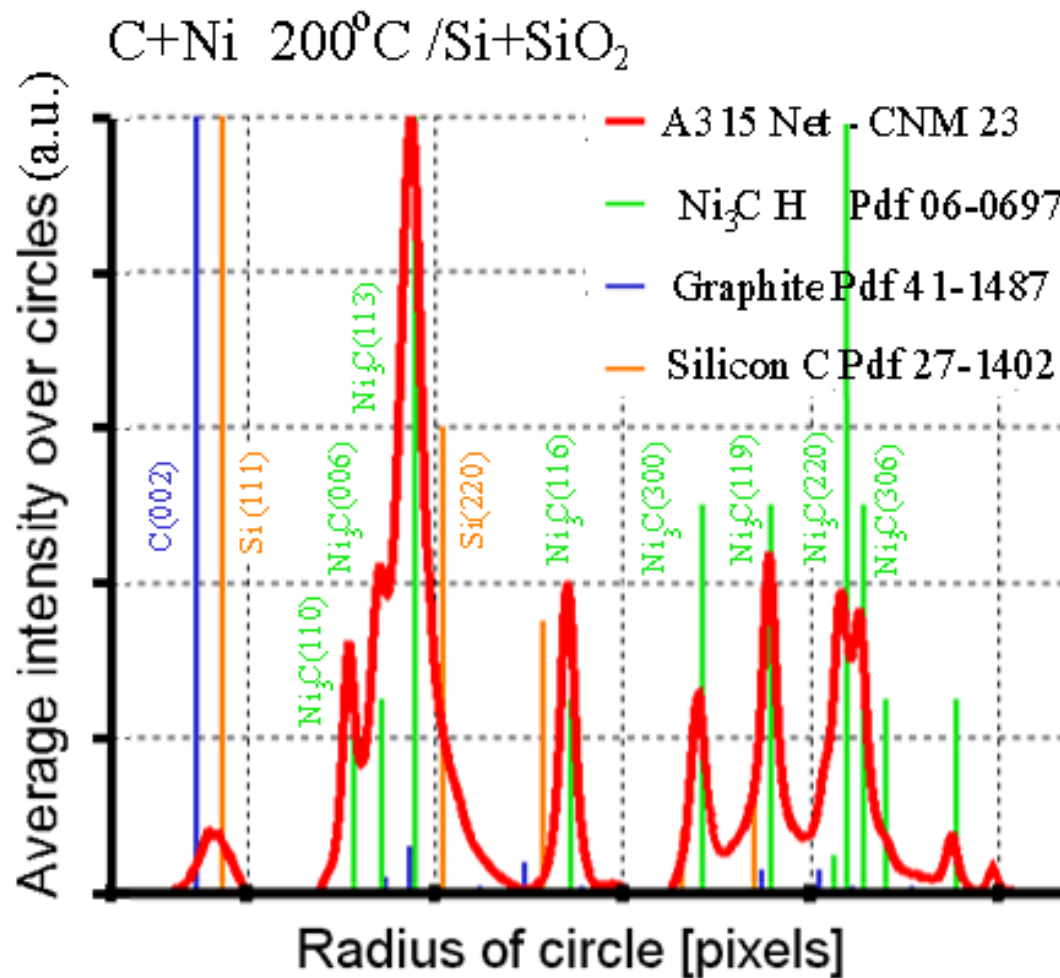
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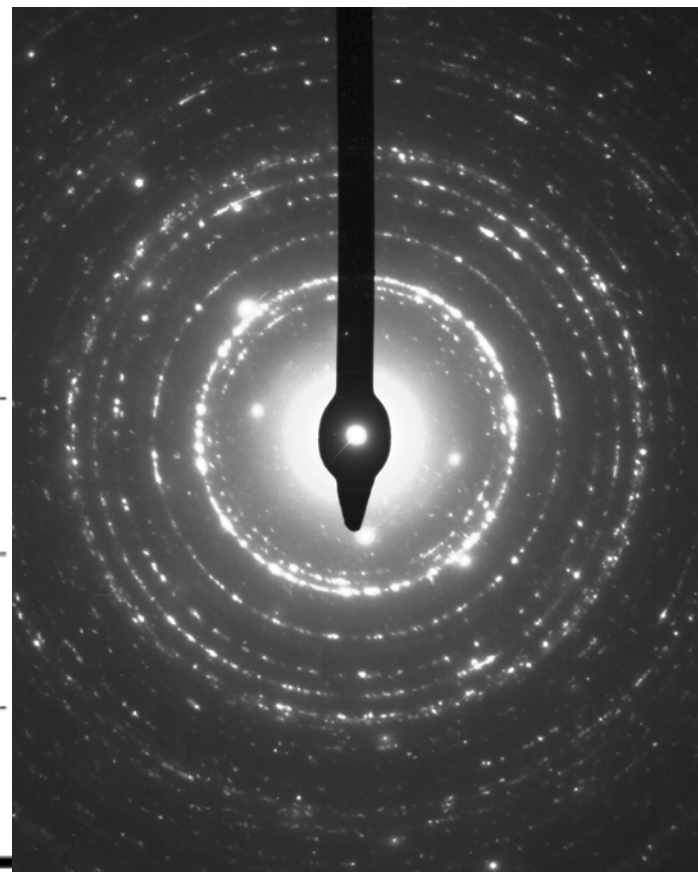
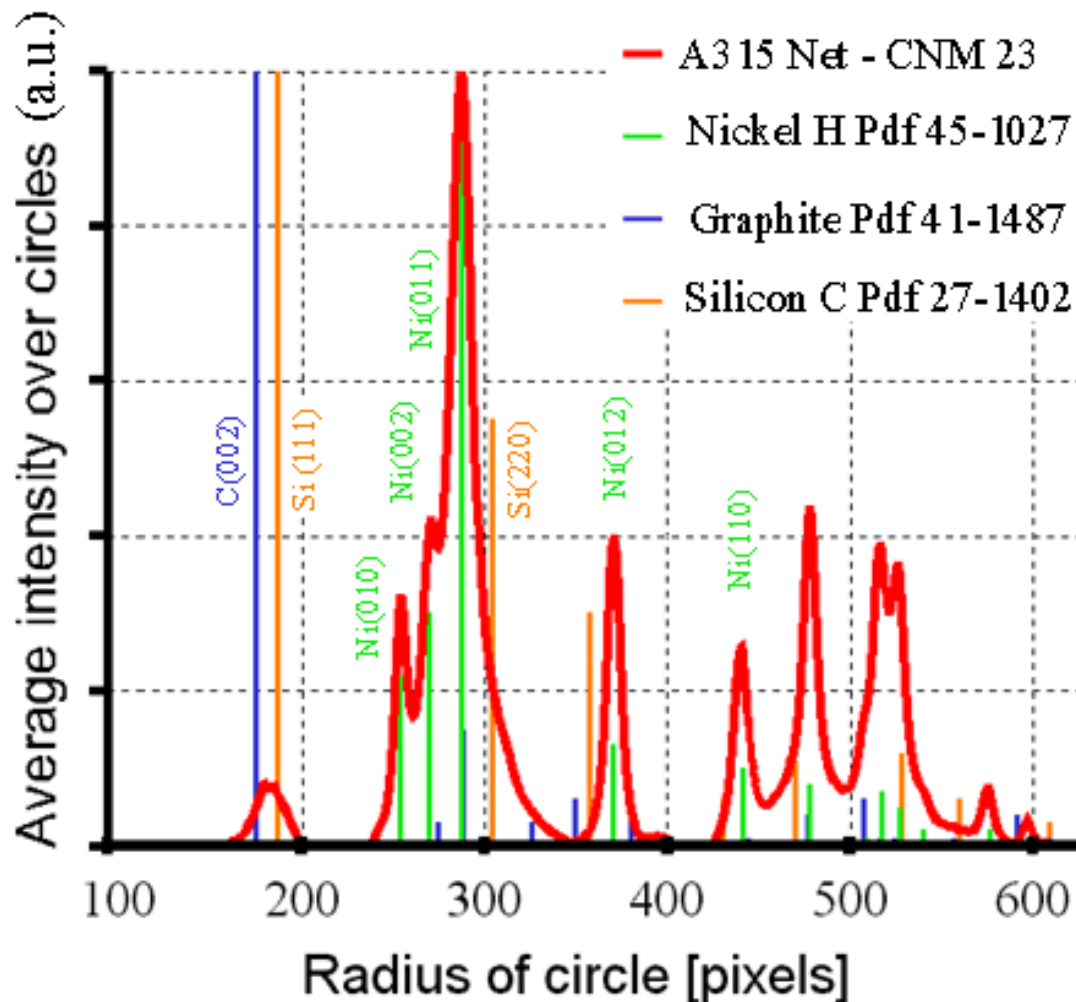
50 nm



Hexagonal Ni/Ni₃C
Graphite-like C

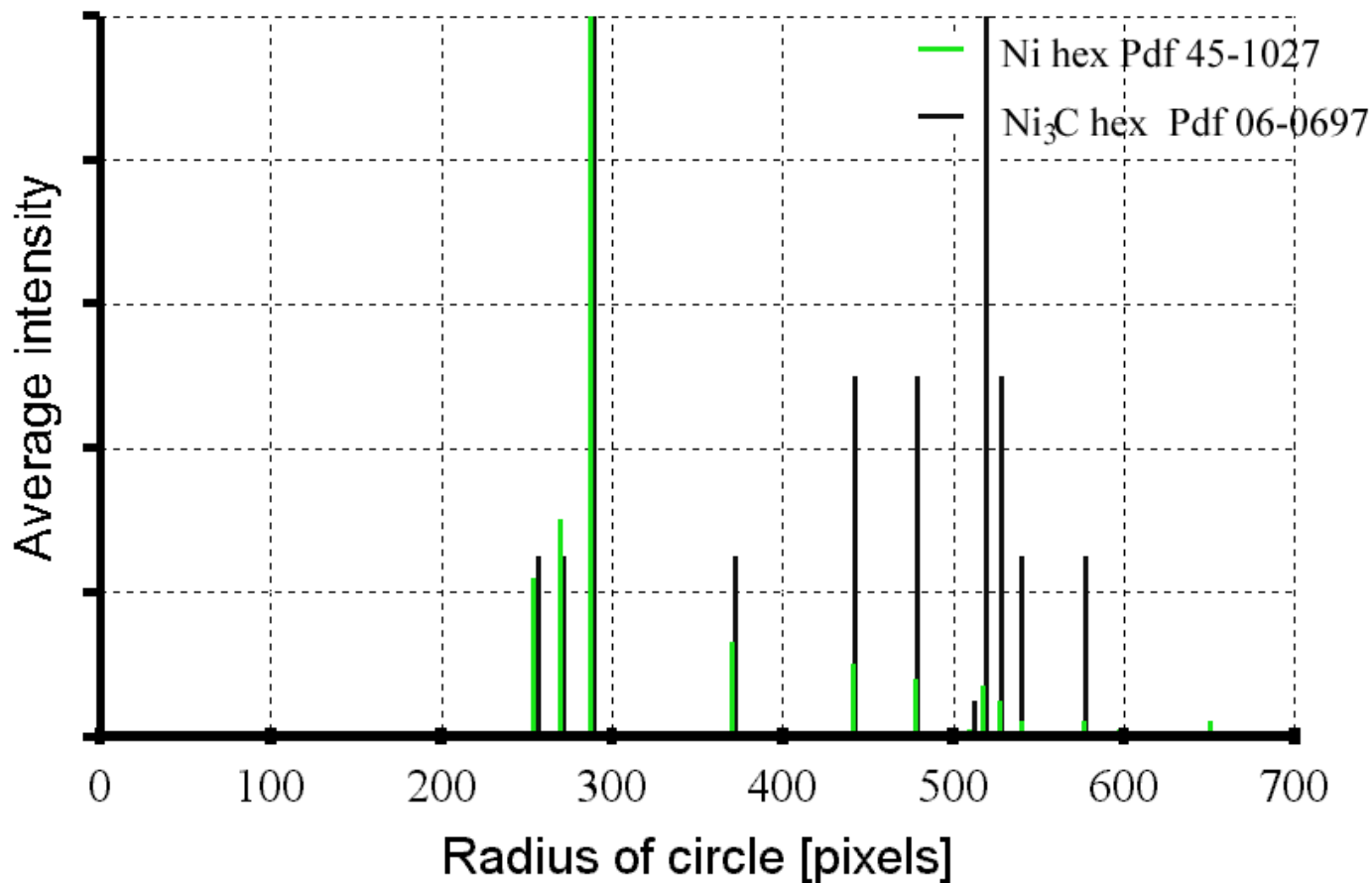


C+Ni 200°C /Si+SiO₂



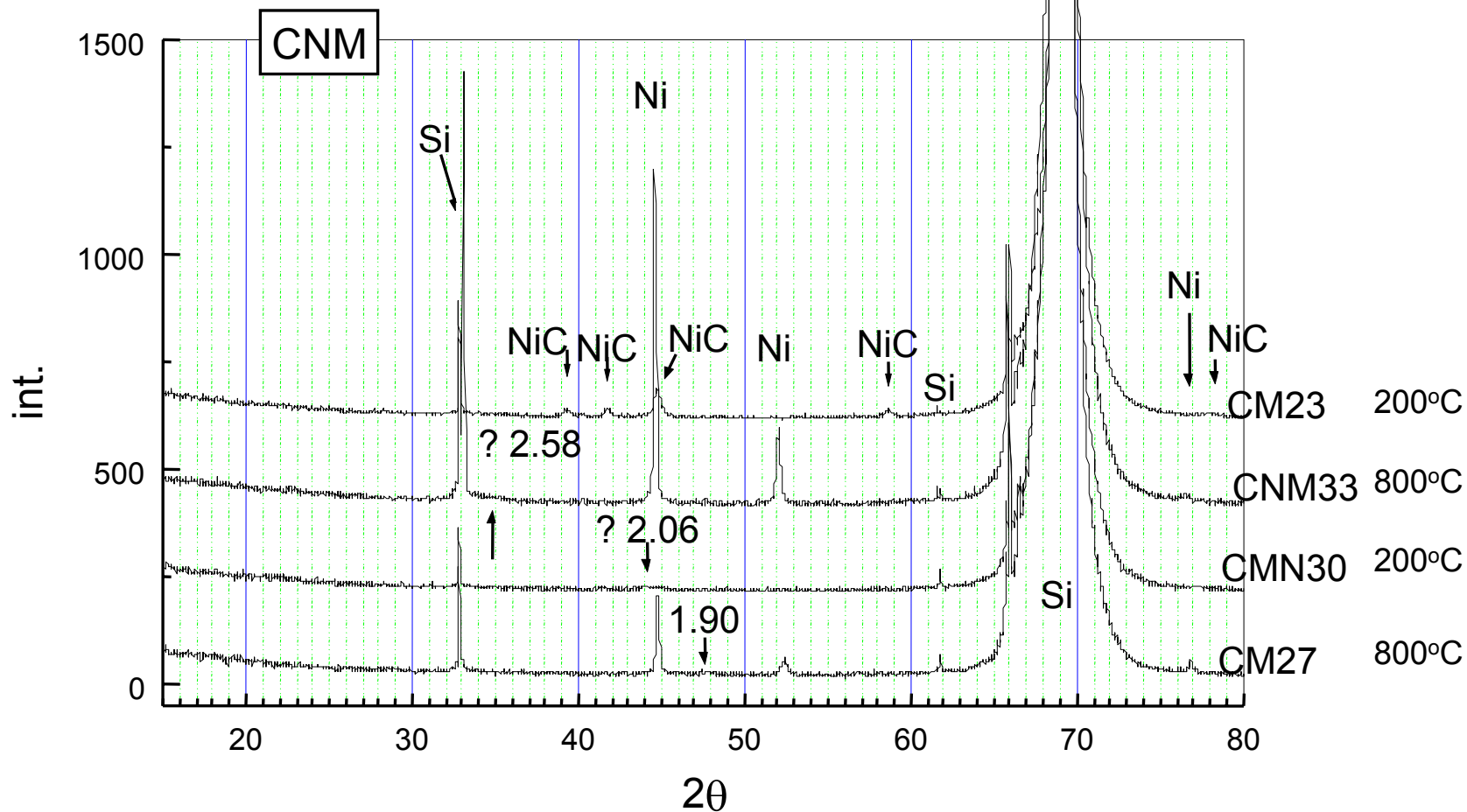


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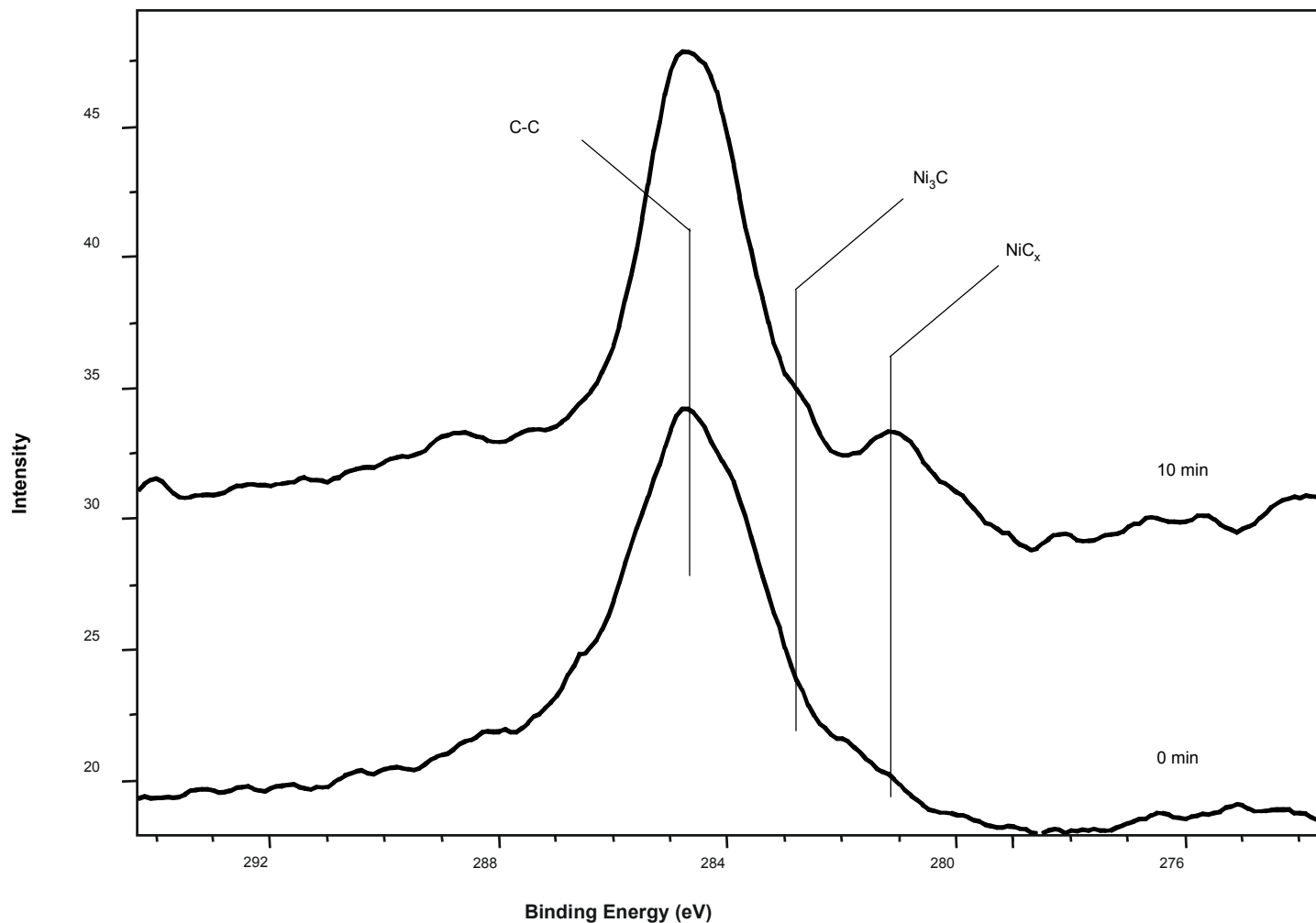


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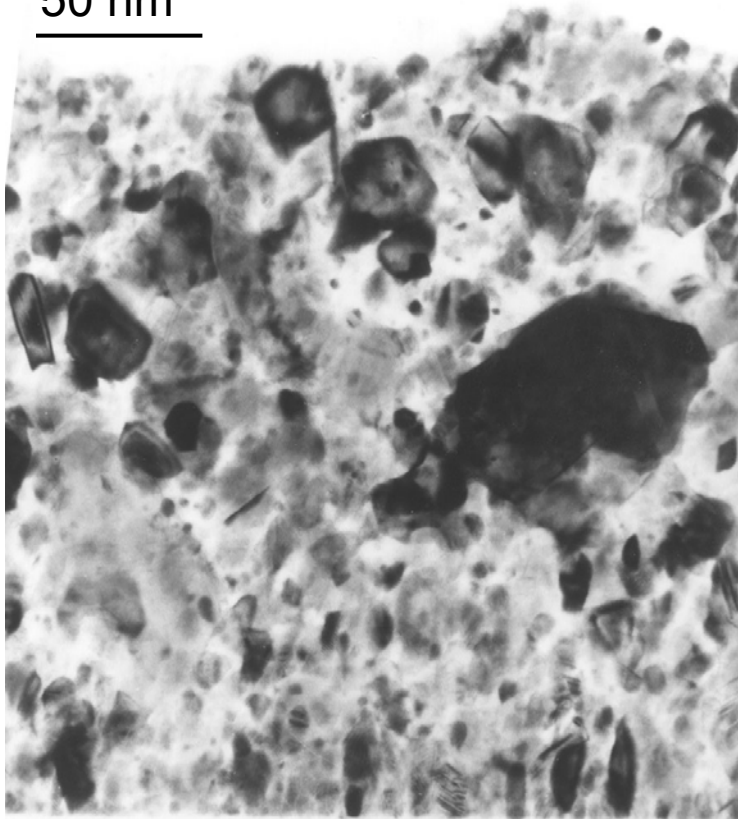


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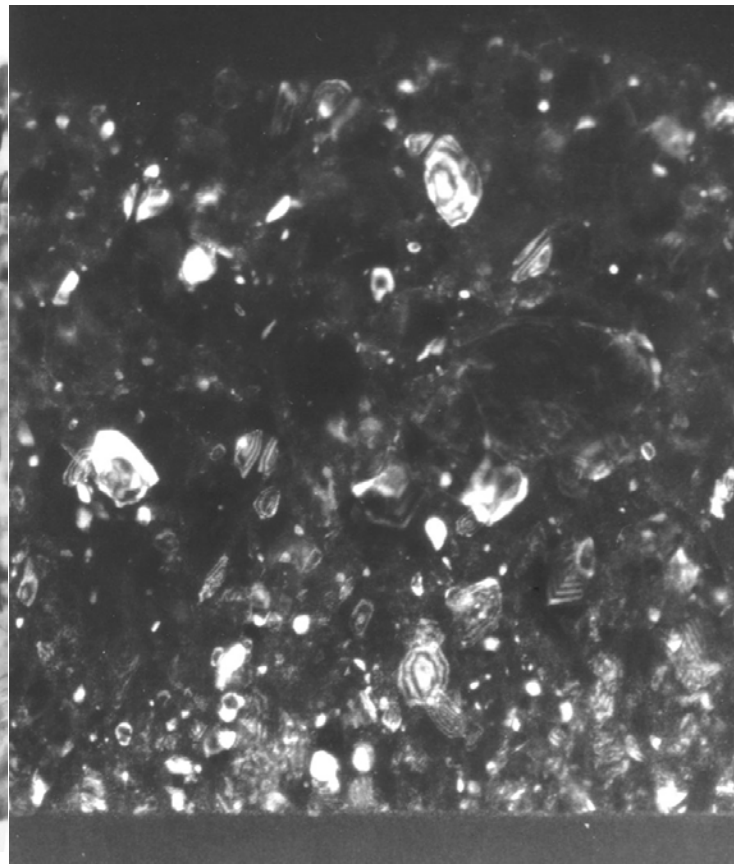


XP spectra of the C1s region of a C-Ni sample deposited at 280°C before and after Ar⁺ ion etching.

50 nm



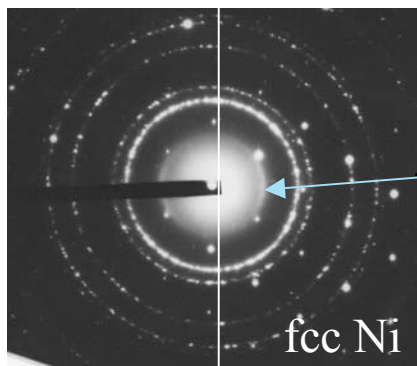
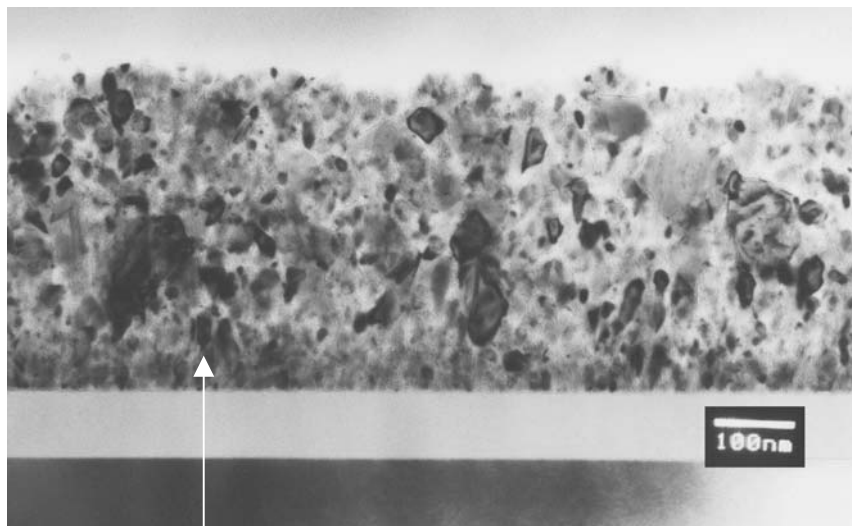
C+Ni(30 at%)
800°C/SiO₂ substrate



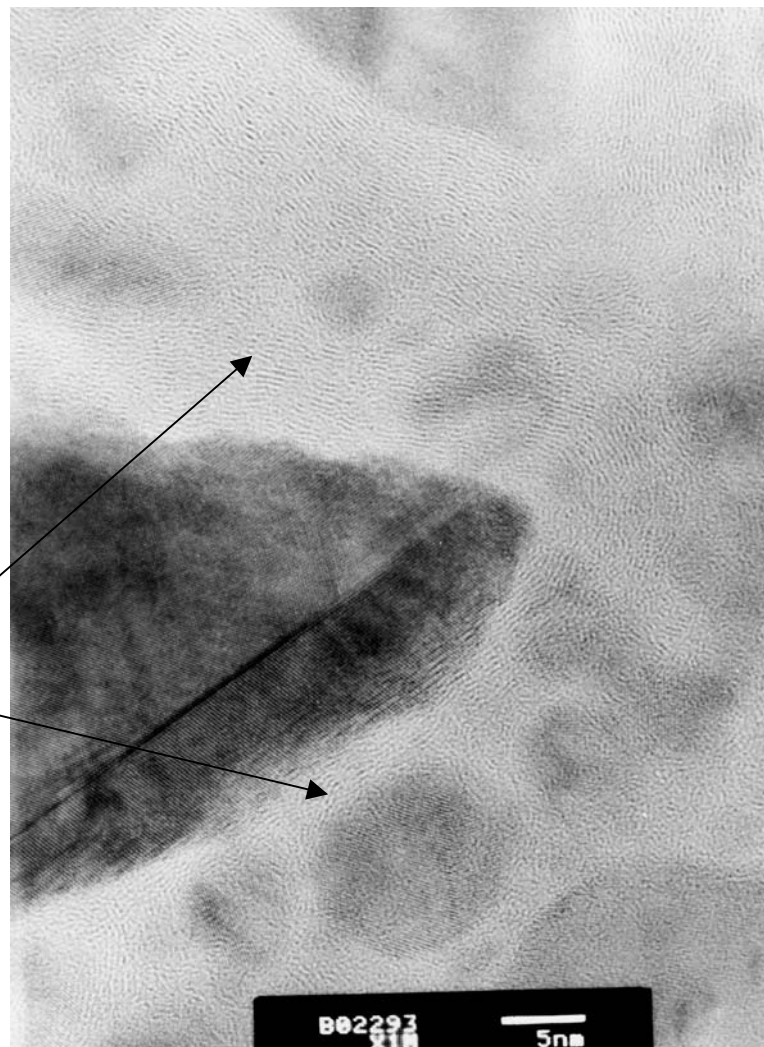
fcc Ni
Graphite-like C



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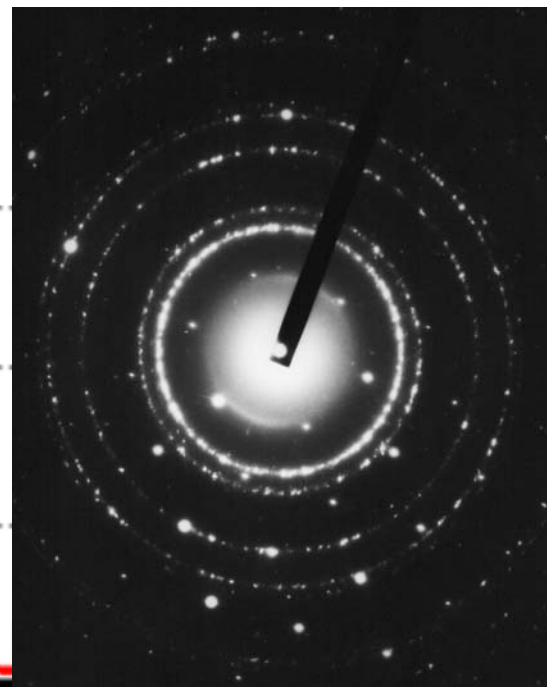
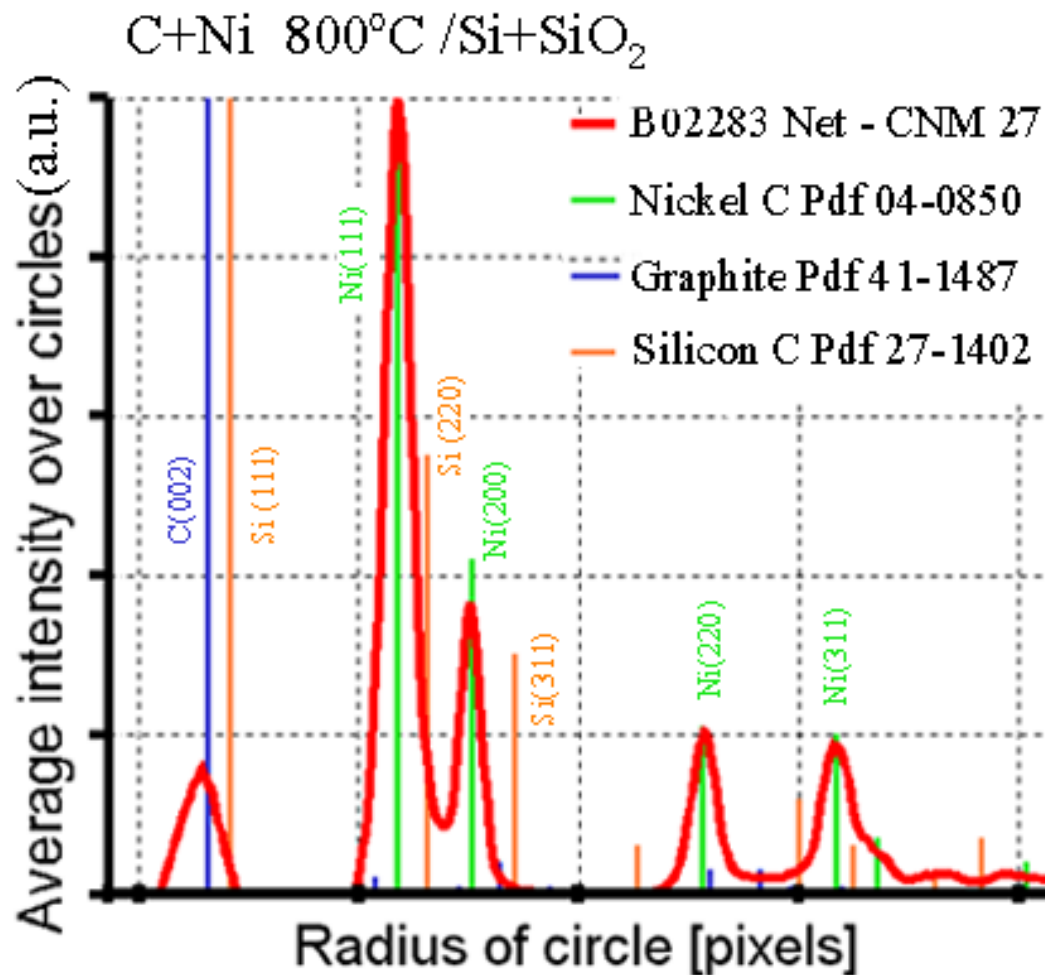
Graphene sheets



C+Ni
800°C/SiO₂ substrate

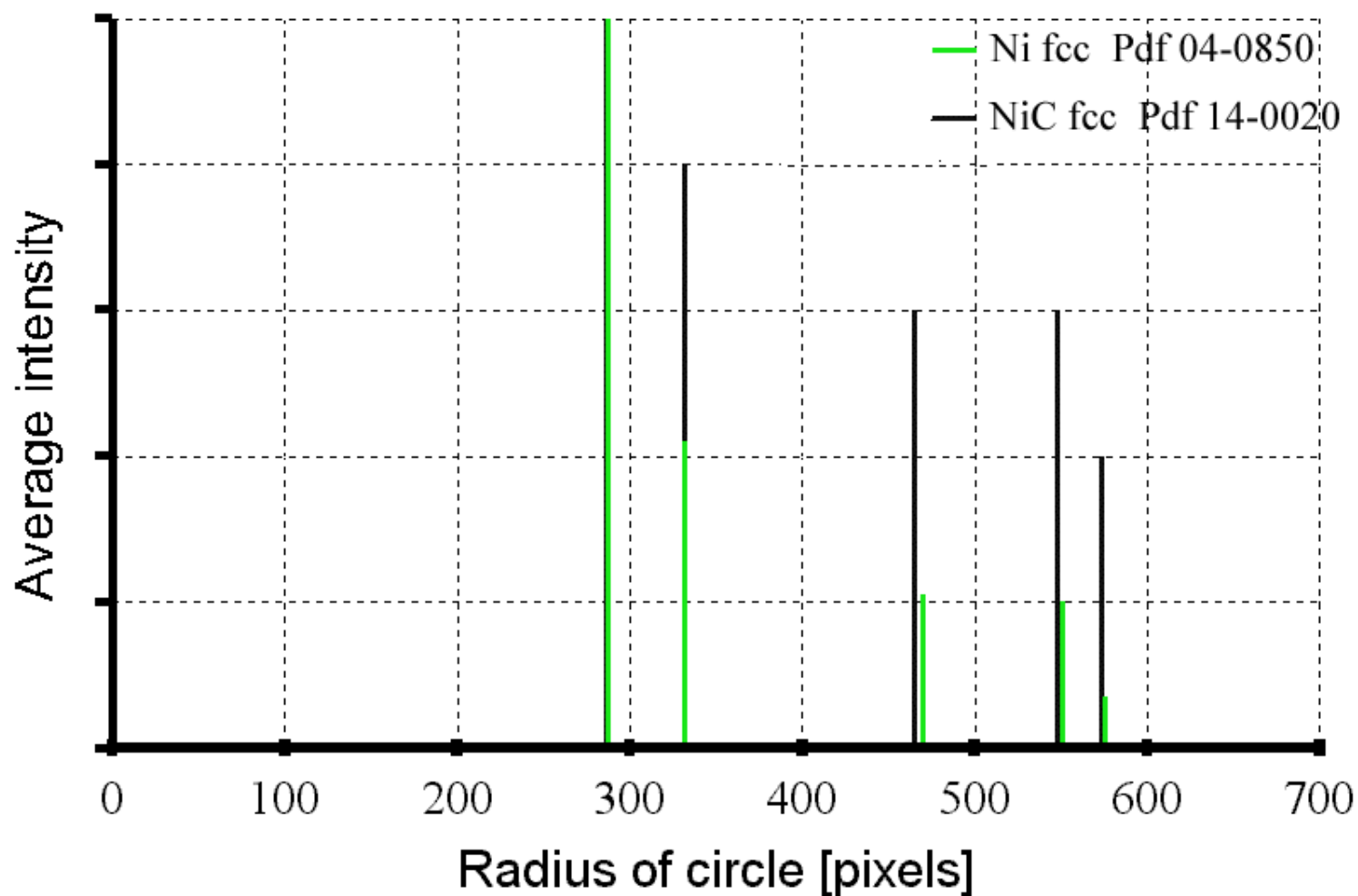


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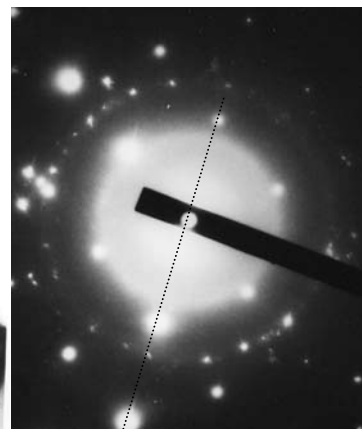
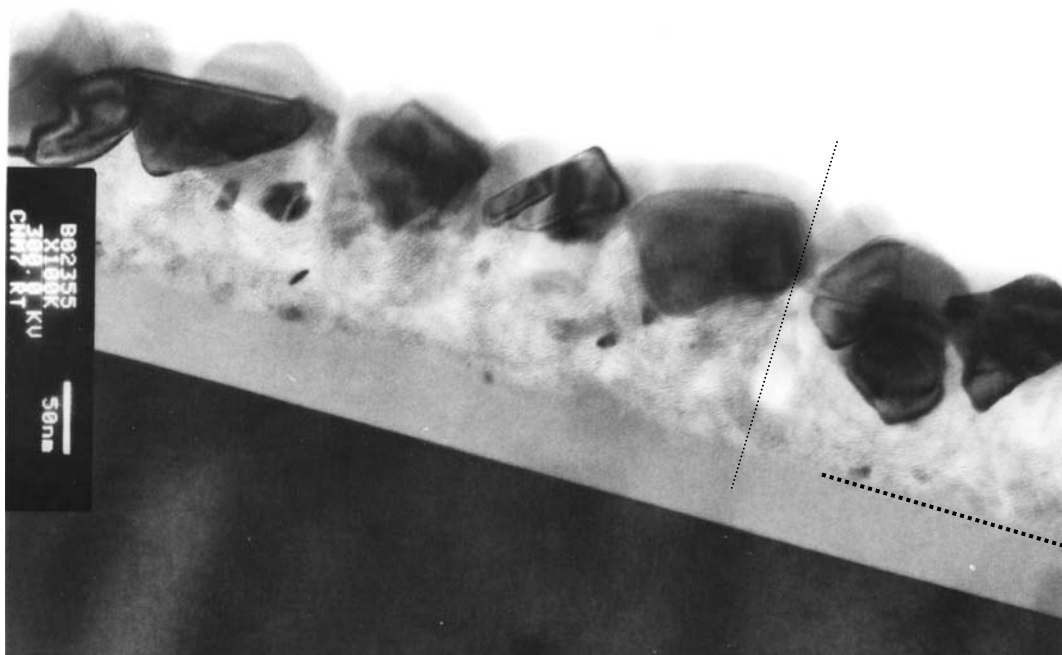


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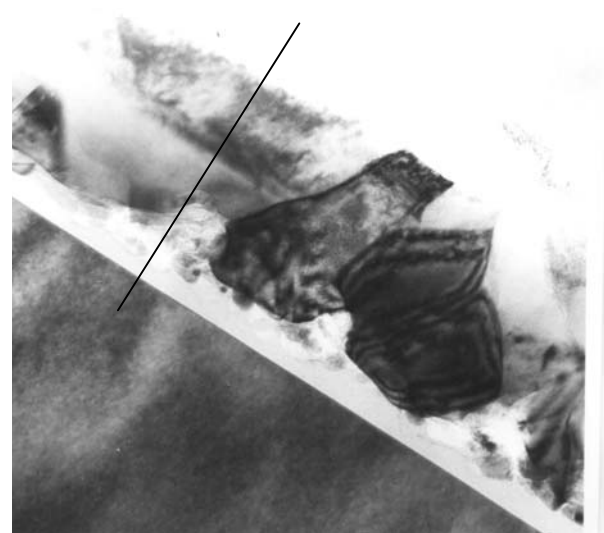
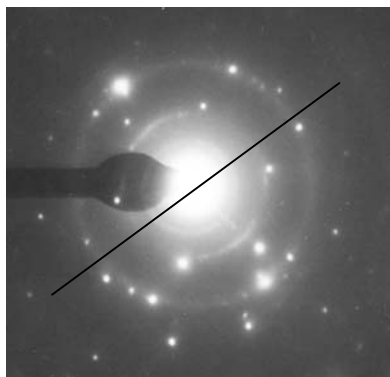
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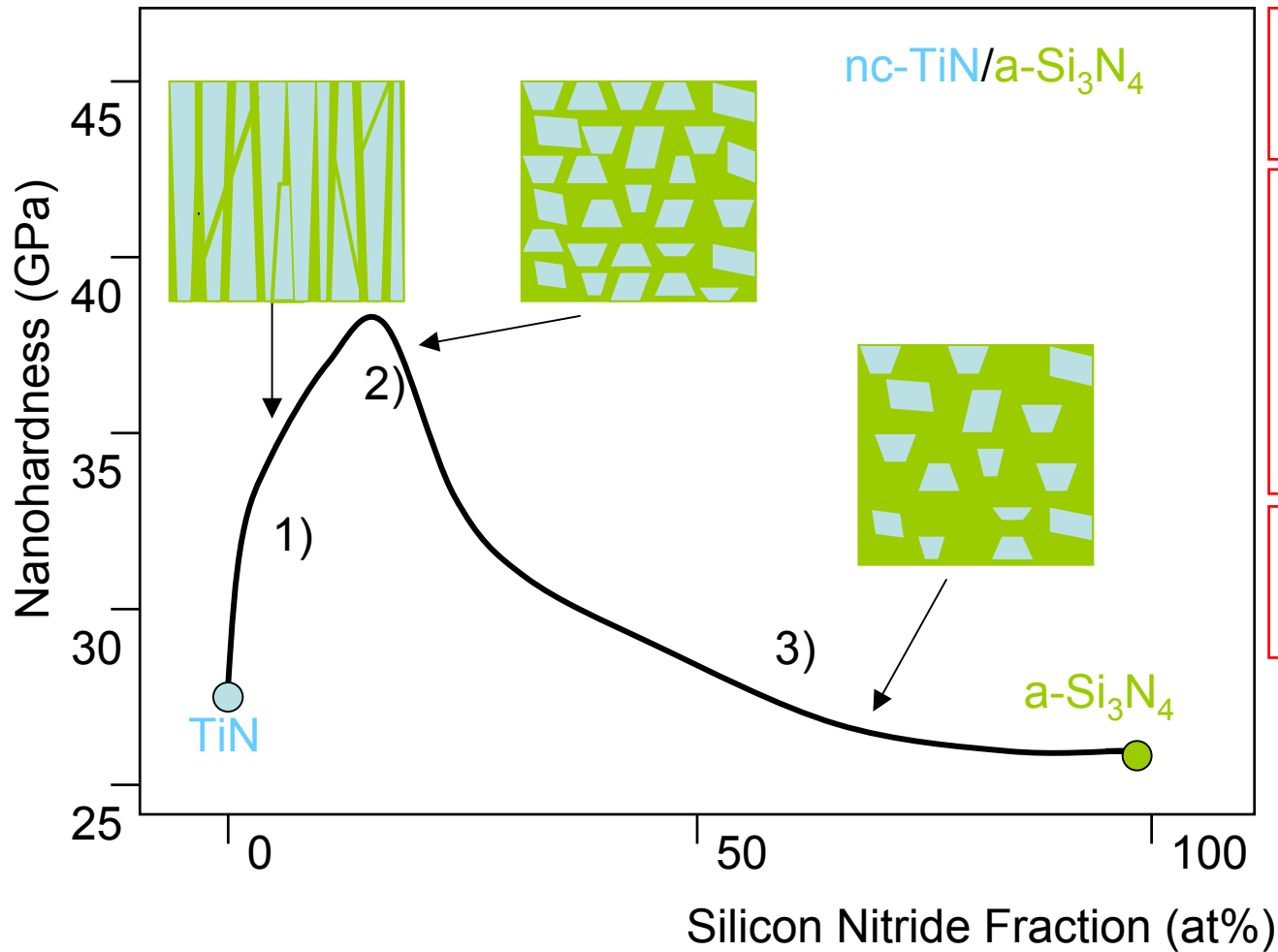


CNM32, 600°C,
B02355, B02357

C+N+Ni

CNM 33
800°C
E499
E505





1) Decrease of TiN grain size due to Si₃N₄ addition.

2) Secondary nucleation of TiN, formation of ncTiN, sharp, thin phase boundaries. Deformation by GB sliding.

3) Thick, deformable Si₃N₄ between TiN grains.



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The essence of the above picture: nanohardness is determined by the morphology of the film.

Compositional changes are not necessary, the deposition parameters and the induced by them self-organizational processes will lead to given morphologies, we observed in C/CNx-Ni films.

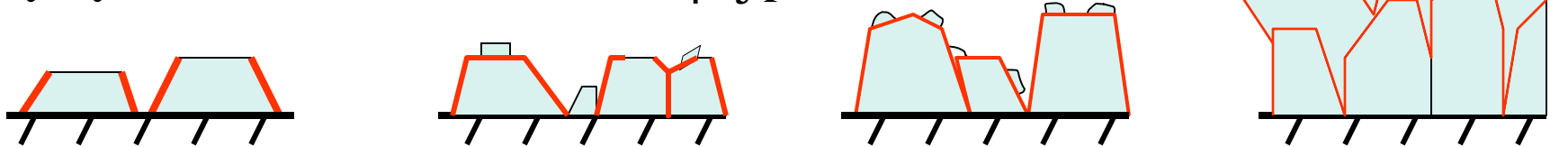
Al-C films: separation of the components according to the thickness and deposition rate of the films.

Formation mechanism of composit structures in co-deposited Al - C film: dependence of composition

$C_{conc} < 0,2$: primary nucleation and growth of Al crystals

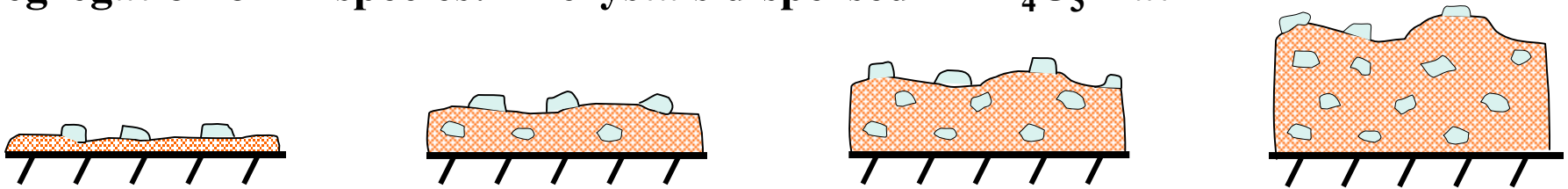
*segregation of C by Al crystal growth, nucleation and growth of Al_4C_3 phase in BD layer on Al crystal surfaces,

*polycrystalline Al structure with Al_4C_3 phase at GB-s

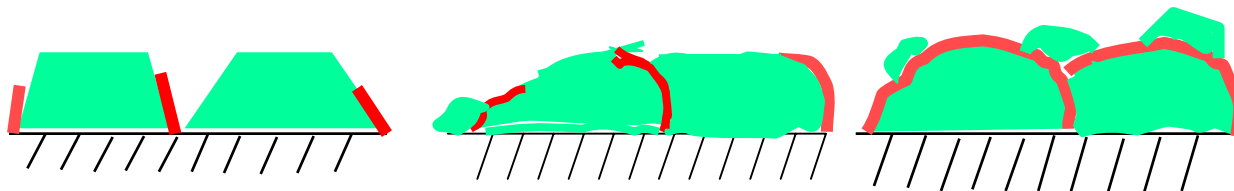
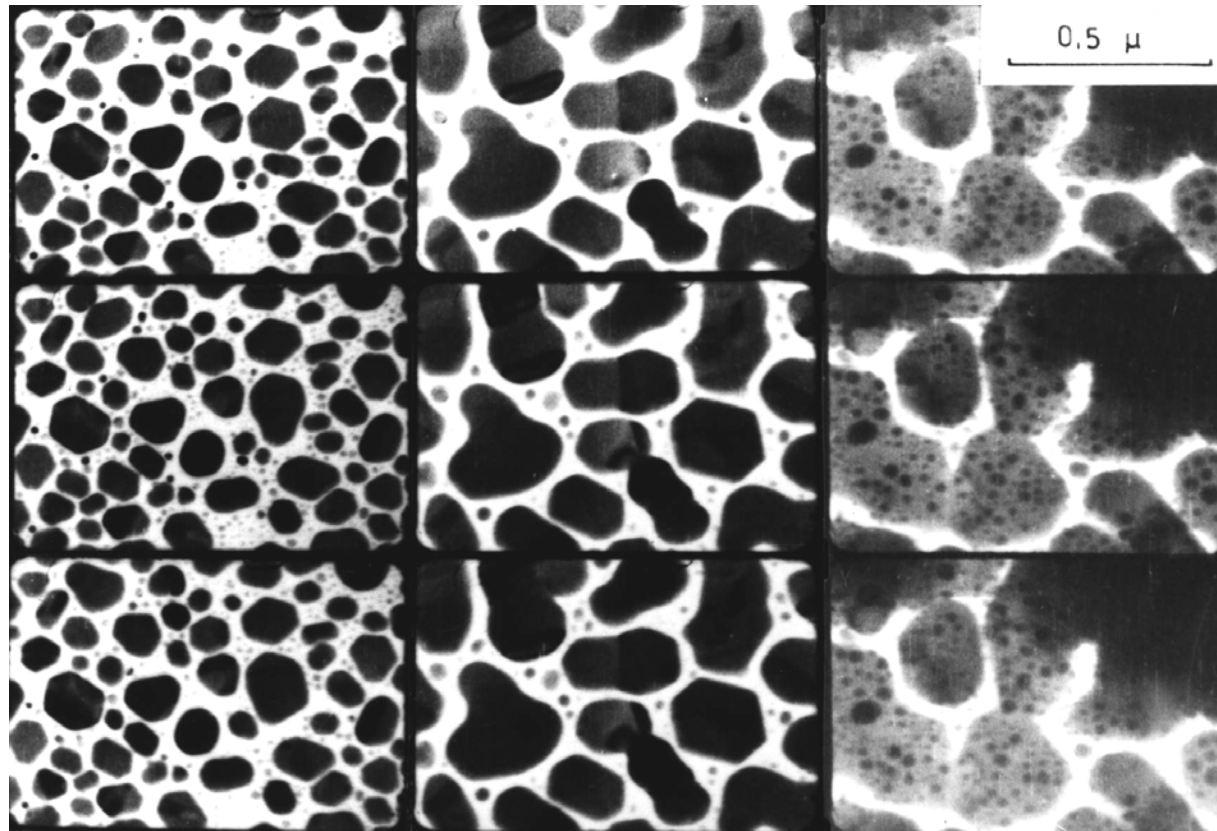


$C_{conc} > 0,2$: primary nucleation and growth of Al_4C_3 phase

• segregation of Al species: Al crystals dispersed in Al_4C_3 matrix



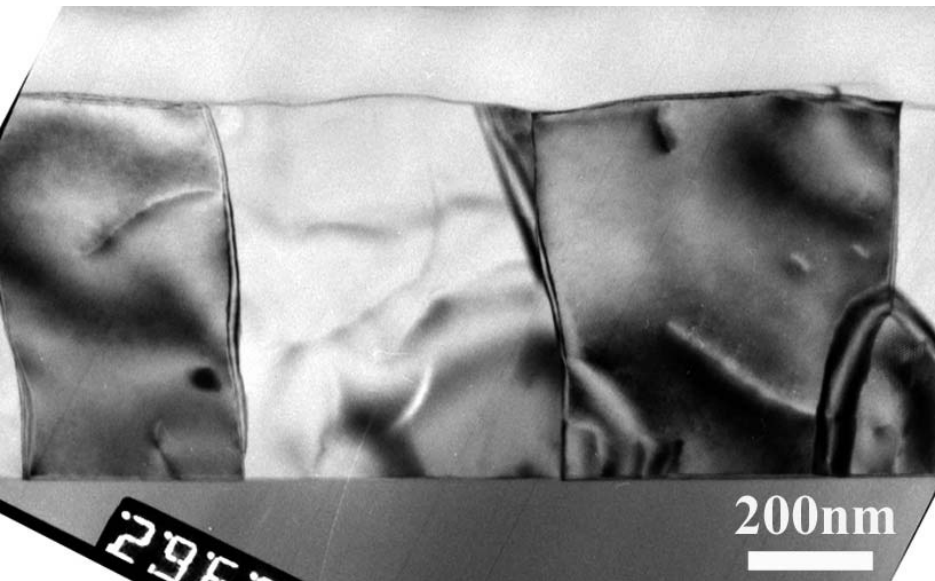
Process induced segregation of co-depositing carbon species results in the formation of a surface covering layer on the growing In crystals
Rounding of crystal shapes ; repeated nucleation of In on the carbon layer covering completely the surface of In crystals (in-situ TEM experiment, $T_s=75\text{ }^{\circ}\text{C}$ J.F.Póczy et al., Japan JAP, Suppl. 2. Part 1, (1974) 525)



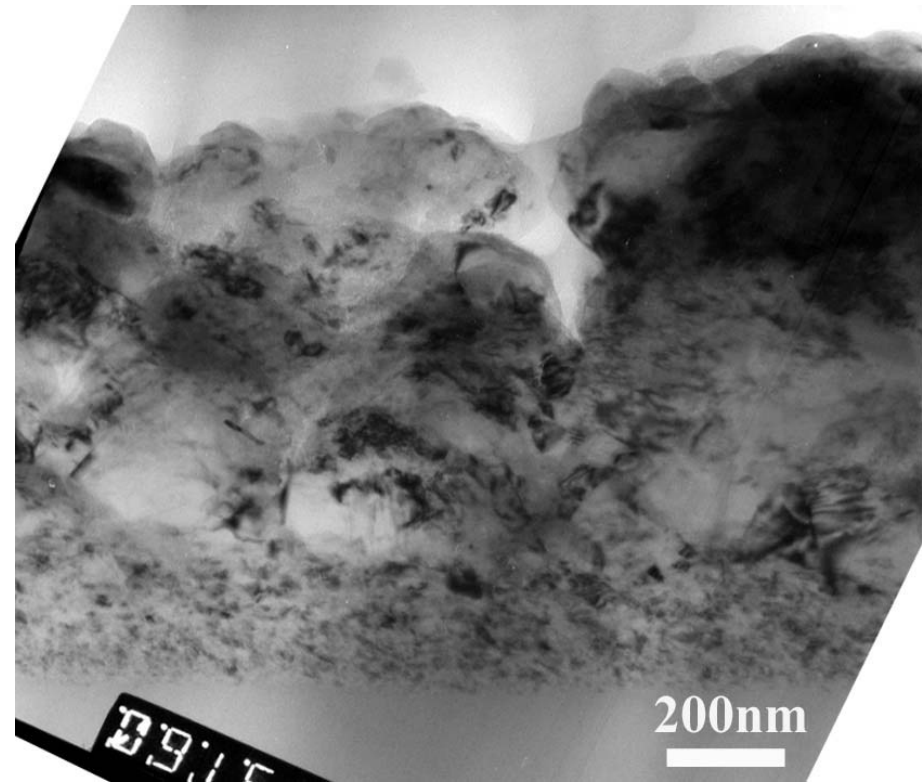
Problems: to understand the mechanisms operative in the development of peculiar composite structures (e.g. nanocomposite, lamellar) in multicomponent thin films.

Present work: dedicated experiments on two-component model system:
codeposited Al and C.

Cross section of Al films with 0 and ≈ 25 at% C, deposited at room temperature

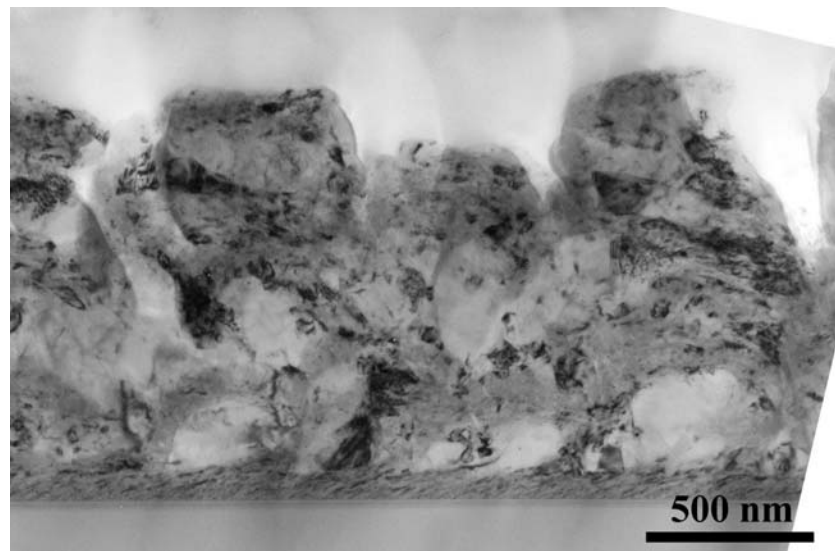
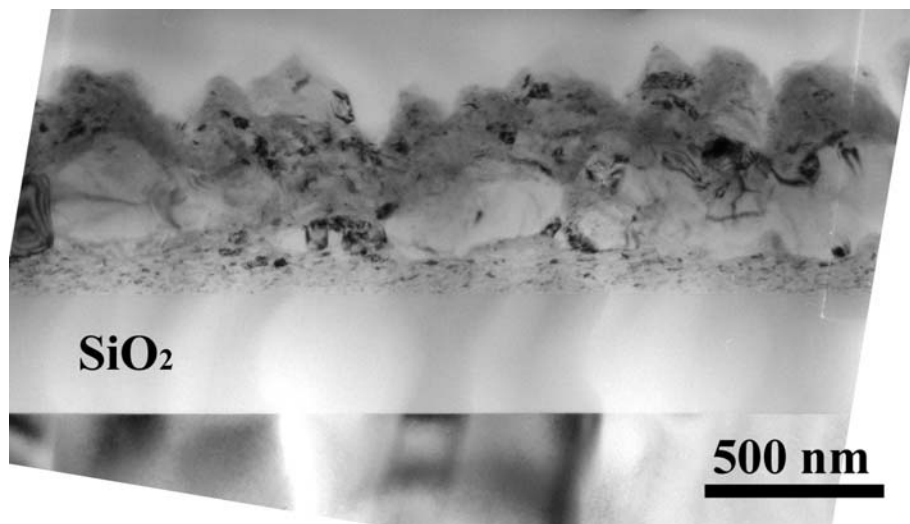
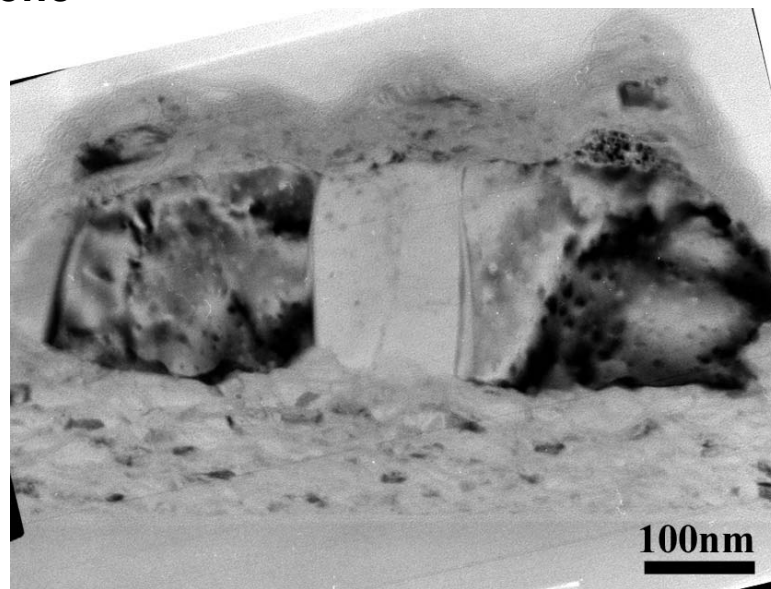
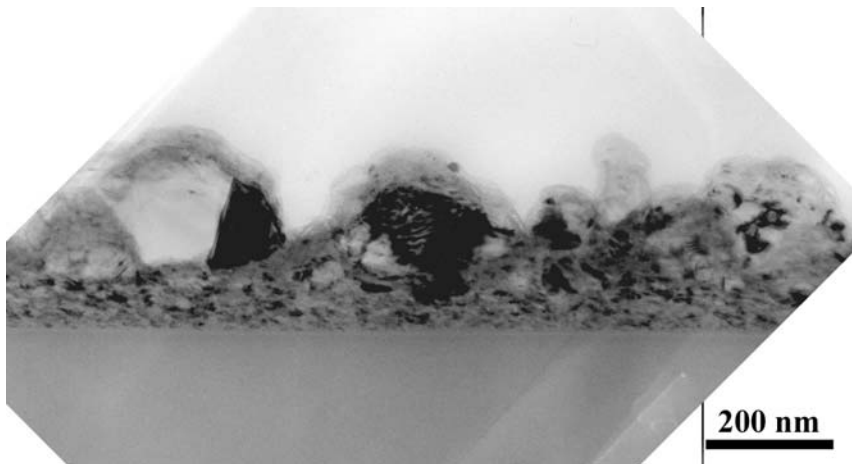


C = 0 at%



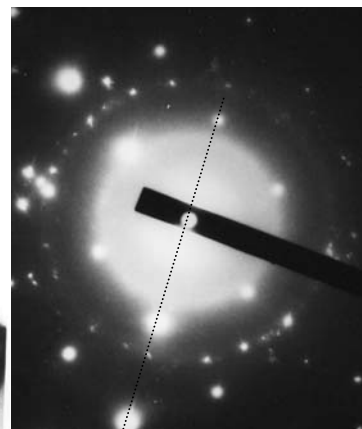
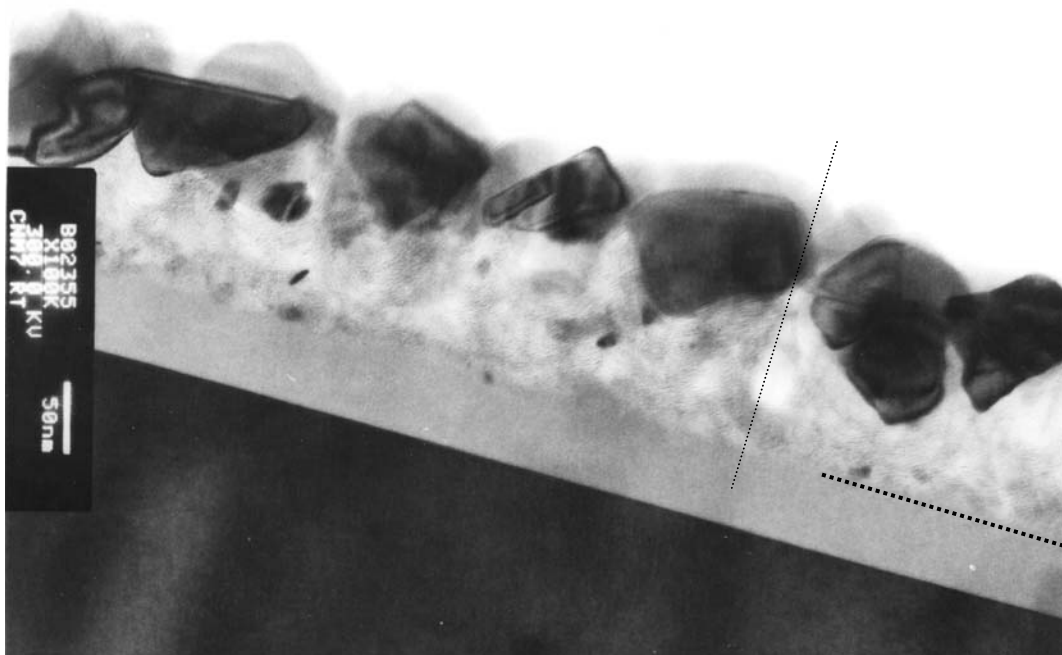
C \approx 25 at%

Cross sectional images of codeposited Al-C films with thickness ($C_{\text{conc}} \approx 25 \text{ at\%}$)





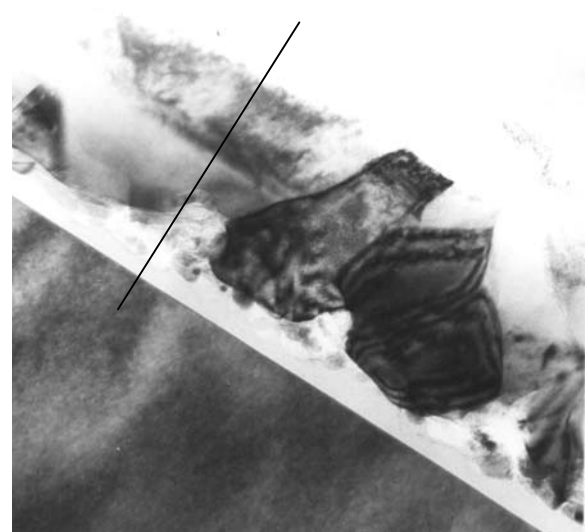
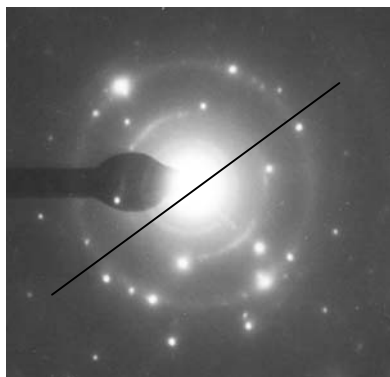
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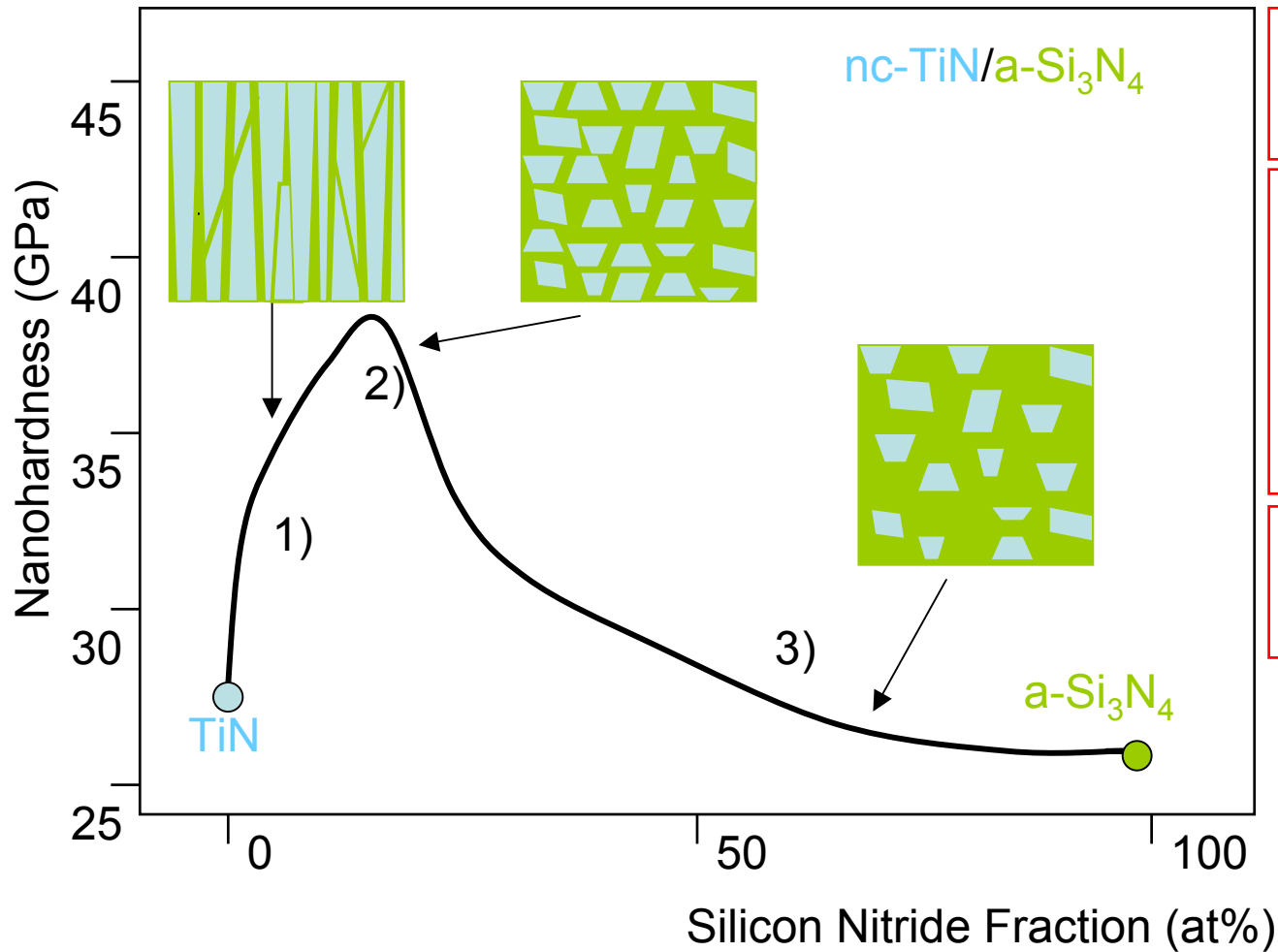


CNM32, 600°C,
B02355, B02357

C+N+Ni

CNM 33
800°C
E499
E505





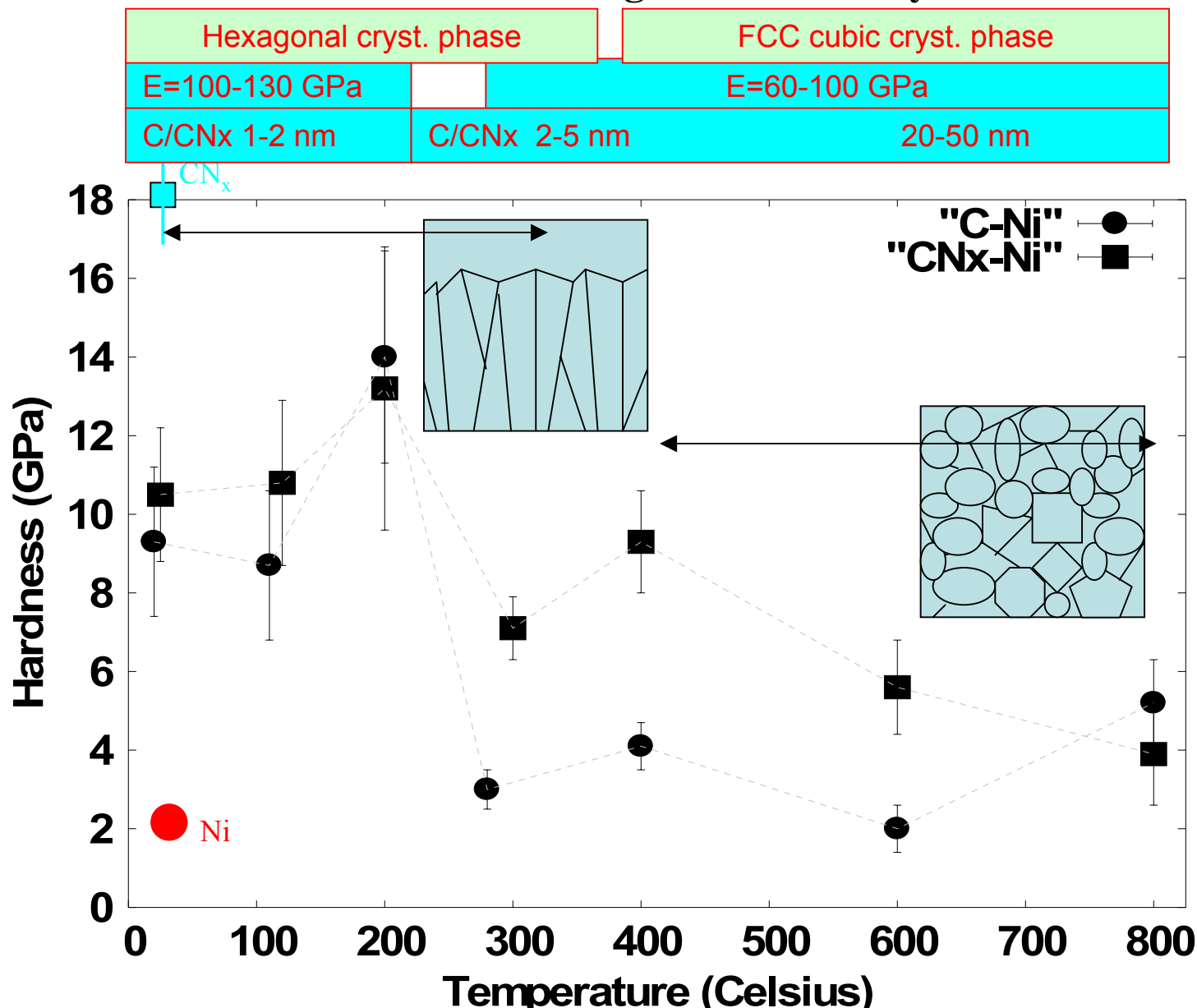
1) Decrease of TiN grain size due to Si₃N₄ addition.

2) Secondary nucleation of TiN, formation of ncTiN, sharp, thin phase boundaries. Deformation by GB sliding.

3) Thick, deformable Si₃N₄ between TiN grains.



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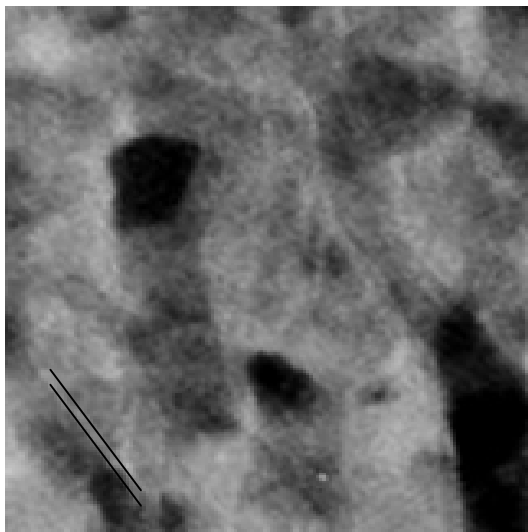


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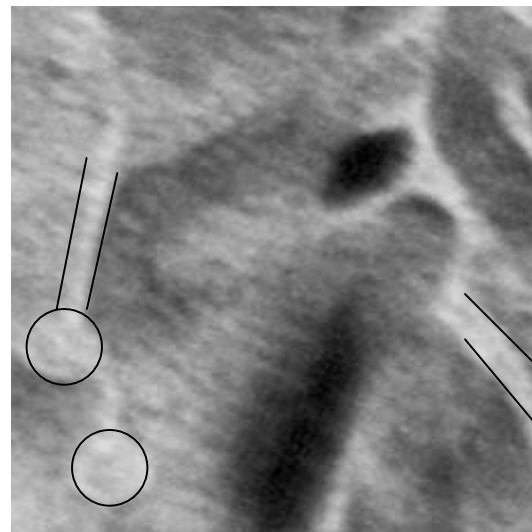
120°C



200°C



300°C



2 nm

$2 \text{ nm} > t$

$d \sim 2 \text{ nm}$

$2 \text{ nm} > t$

$d \sim 2-4 \text{ nm}$

$t = 2-5 \text{ nm}$

$d \sim 10 \text{ nm}$

C+N+Ni



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4. Conclusions

-The major part (80-90 vol %) of the films is crystalline. On the basis of XPS and ED data, for films deposited below 400°C the hexagonal crystalline phase was assigned to Ni_3C , while above 400°C it is changing to fcc structured Ni, and NiC_x .

-The crystalline grains form a columnar morphology below 300°C which gradually changes to a globular one as the growth temperature increases. From 600°C a separation of Ni into a layer of large grains of fcc metallic phase was observed.

-The matrix of the films deposited between 20-200°C can be described as a 1-2 nm thick amorphous carbon/ CN_x , separating the crystalline columns of elongated Ni_3C grains. From 200°C, the C/ CN_x matrix gradually becomes graphitic-like and at least 2-5 nm thick layers appear around the crystalline grains. At higher temperatures the C/ CN_x matrix becomes thicker and more ordered.

-Nanomechanical properties show a distinct dependence on the deposition temperature. Films deposited at 20-200°C possess the highest hardness up to 14 GPa. The lowest friction coefficient was measured for films deposited at 400-600°C. Generally, the CN_x -Ni films have higher hardness and elastic modulus but lower coefficient of friction than their C-Ni counterpart films probably due to nitrogen cross-links between graphitic layers. The decreasing of the hardness at 300°C is most probably due to the thickening of C/ CN_x matrix between the crystalline grains



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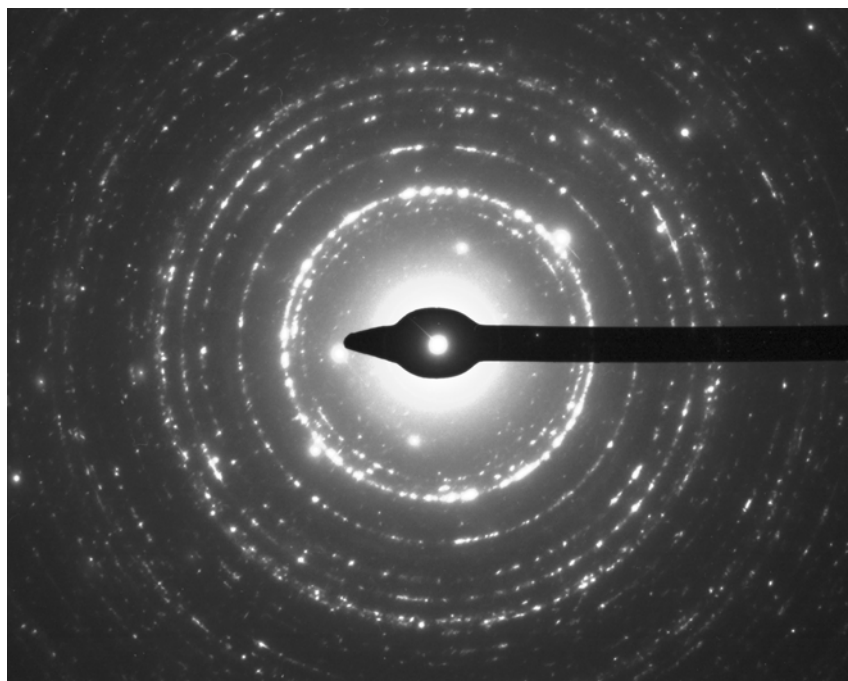
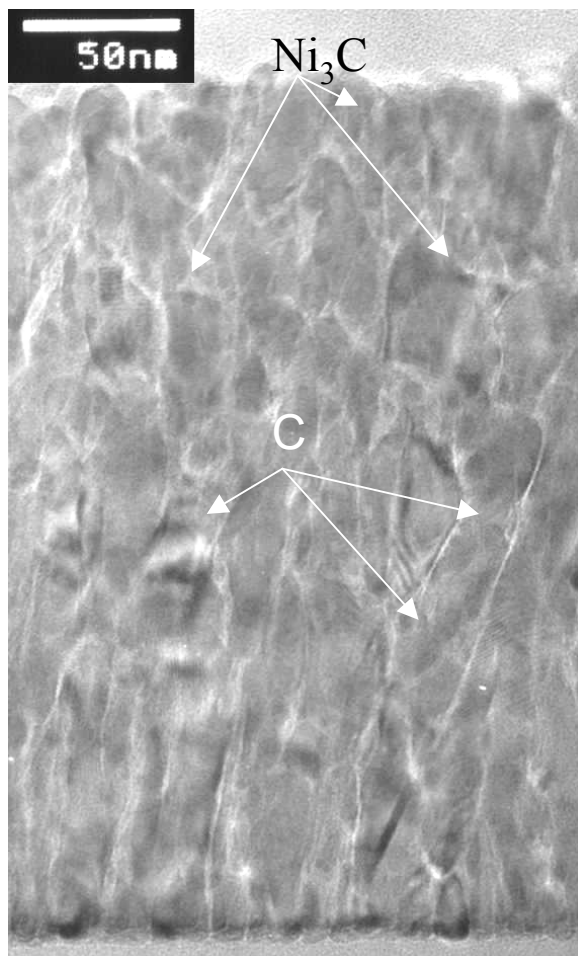
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THANK YOU FOR THE ATTENTION

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4. CONCLUSIONS

C-Ni and CN_x -Ni films of 10-30 and 200-300 nm thickness were deposited by d.c. magnetron sputtering onto SiO_2 and NaCl substrates, between 20 and 800 °C substrate-temperatures. The nanocomposite is composed from mostly fullerene-like matrix of C or CN_x and a crystalline phase undergoing a phase change at 400 °C growth temperature from hexagonal Ni/Ni₃C to fcc Ni phase. Generally, the CN_x -Ni films have higher hardness and elastic modulus than C-Ni films.

The films deposited at 20-200 °C can be described as columnar, fine structures of elongated grains of hexagonal Ni/Ni₃C embedded into an amorphous or partly ordered to graphene sheets matrix of uniform (1-2 nm) thickness between the crystalline grains. These films have hardness of 9-14 GPa and elastic modulus of 100-130 GPa.

Above 200 °C Carbon and CN_x become more fullerene-like. With increasing substrate temperature the thickness of C/ CN_x matrix between the fcc Ni crystallites becomes nonuniform (2-20 nm thick). The crystalline (fcc) Ni becomes globular with a broad size distribution ranging from 5 to 100 nm in diameter. The films get softer, hardness goes down to 2-6 GPa the elastic modulus being between 60-100 GPa.

The changes in the hardness can be prescribed partly to the differences of the moduli of the obtained material as well as to the morphology of the film. The columnar fine grain structures and uniformly thin matrix walls together with the higher values of the moduli result in higher hardness values.